

GEMP-190m
(INFORMAL)

69p
N 64 33783

FACILITY FORM 808

(ACCESSION NUMBER)

(THRU)

(PAGES)

(CODE)

(NASA CR OR TMX OR AD NUMBER)

(CATEGORY)

OTS PRICE

XEROX

\$

3.00

MICROFILM

\$

0.25

Nuclear Materials & Propulsion Operation

INTRODUCTION TO NUCLEAR PROPULSION

Lectures 19 and 20 - RADIATION DAMAGE AND EFFECTS

J. R. Beeler, Jr.

NASA CR 52949

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RADIATION DAMAGE AND EFFECTS

Lectures 19 and 20

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*Done or others
in this series*



May 7, 8, and 9, 1963

Prepared for the George C. Marshall
Space Flight Center of the National
Aeronautics and Space Administration

(NASA

Contract No. NAS8-5215)

FOREWORD, ACKNOWLEDGEMENTS AND REFERENCES

In these notes radiation damage and effects in organic materials are treated more completely than that in metals, ionic crystals and semiconductors. This emphasis exists because the interests of the RIFT Program appear to be best satisfied by such a treatment. The author is indebted to Colonel Scott Fellows, Captain R. D. Hensley, Adrian Clark, Frank Magliato, Rex Morton, Aubrey Smith and Lowell Zoller, of the Marshall Space Flight Center, for their help in defining what should be the content of these notes. Stimulating discussions with Colonel Fellows, Mr. Magliato and Mr. Zoller were particularly helpful. The considerable amount of time these gentlemen spent in explaining to me the ideas pertinent to the RIFT Program is deeply appreciated. A major part of the material on organic materials (Sections 6 and 7) is a condensation and rearrangement of material from Reference 4.

The presentation of fundamental ideas is the basic intent of these notes. References 1 and 2 provide information which defines the pertinence of radiation damage and effects concepts to RIFT and the radiation environment in which the system will operate. Reference 5 provides an exhaustive treatment of radiation chemistry for organic materials and References 6 - 16 provide background material which describes the theoretical and experimental state of radiation studies for inorganic materials. Graphite is treated in References 9 and 10. Reference 3 is probably the best reference to start with. After that look at References 9 and 10. A good solid state physics background can be obtained by reading References 11 - 13. References 14 and 15 cover the "old" dislocation work, and Reference 16 talks about the newer ideas in this field.

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1. INTRODUCTION

1.1 LOCALIZED ENERGY DEPOSITION

Physical, chemical and nuclear changes are produced in a material as a consequence of exposure to radiation. There are two major classes of radiation-induced changes: (1) primary effects (radiation damage) produced directly in the initial interaction(s) of radiation with the constituents of the material, and (2) secondary effects (radiation effects) which arise from the interaction of radiation damage products. For the moment consider radiation in the general sense - energy moving through vacuum or matter - and put aside considerations of the particular forms radiant energy may assume. Also consider matter in the general sense; consider it to be a collection of individual atomic or molecular structural units which are bound together by attractive forces. The essential idea involved in radiation damage and radiation effects theory is that when radiation energy is locally deposited in a material, in such a way as to break up the bonds between its structural units, the material will come apart in this local region. It is also possible that the individual structural units themselves can be broken up or changed in some manner as a result of this localized energy deposition. This constitutes the primary effect of exposure to radiation. The secondary radiation effects pertain to what happens when the displaced structural units rearrange themselves and/or when displaced structural units, altered structural units and fragments of broken structural units interact in an effort to achieve an equilibrium state.

One sees immediately that nearly all facets of physics and chemistry relating to the way a material is held together in its equilibrium state and to the way the constituents of a material grow together in the non-equilibrium process of its formation, are pertinent to a study of radiation effects. For the most part, radiation damage studies are concerned with these two types of changes in an irradiated specimen, i.e., (1) displacement of atoms, radicals and molecules from their normal positions in a material; (2) changes in the electronic states of individual atoms and molecules. Radiation damage refers to changes in an irradiated specimen occurring in a little volume of atomic dimensions (10^{-8} cm). The length 10^{-8} cm is called an Angstrom unit and is denoted by the symbol, A.

On the other hand, radiation effects are changes in the physical properties of an irradiated specimen which can be measured in the macroscopic sense. These macroscopic changes represent the cumulative effect of the multitudinous individual atomic scale rearrangements, caused directly by radiation, which constitute radiation damage. Radiation effects include changes in all properties of matter. One of the major problems in radiation damage research is to identify the particular types of atomic scale radiation damage events which take place in an irradiated specimen from the particular combination, and/or relative magnitudes of the radiation effects they produce. Conversely, another major problem in radiation damage research is to establish the types and relative magnitudes of the radiation effects which can result from a particular type of radiation

damage event. Table 1.1 lists some physical property measurements used in analyzing radiation damage in crystalline solids.

1.2 TYPES OF RADIATION

We will classify radiation types from the standpoint of the radiation particles being charged or neutral.

<u>Charged Particles</u>	<u>Neutral Particles</u>
electrons (β -particles)	photons (light, X-rays,
protons (p)	γ -rays)
deuterons (d)	neutrons
α -particles	atoms
ions	

Protons, deuterons and α -particles are, respectively, hydrogen, deuterium and helium atom nuclei. They are positively charged. Electrons are negatively charged.

<u>Particle</u>	<u>Charge in Electron Units</u>	<u>Mass in Atomic Units</u>
electron	-1	1/1836
proton	+1	1
deuteron	+1	2
α -particle	+2	4

The electronic charge is 4.8×10^{-10} statcoulombs (1.6×10^{-19} coulombs). The atomic mass unit is 1.67×10^{-24} grams. In this discussion ions are atoms heavier than helium which have either more or fewer electrons than their normal complement. A negative ion has more electrons than the normal atom, a positive ion fewer electrons. It is possible for a very fast atom to lose all of its electrons in which case it is referred to as being "stripped" or completely ionized.

Radiation Units

Curie	One Curie is the amount of radioactive material which gives 3.7×10^{10} disintegrations per second (the same number as one gram of radium).
Roentgen	The quantity of X-ray or γ -ray radiation which, when secondary electrons are fully utilized and the wall effect of the chamber is avoided, produces in 1 cm^3 of atmospheric air at 0°C and 76 mm Hg pressure such a degree of conductivity that 1 e.s.u. of charge is measured at saturation current. This is an <u>exposure dose</u> not an <u>absorption dose</u> .
rep	That dose of ionizing radiation which corresponds to an energy absorption of 84 ergs per cm^3 in tissue.

TABLE 1.1

Dimensional Measurements

macroscopic length
lattice constant (X-ray)
total mass
mass density

Electrical Measurements

resistivity
dielectric constant
Hall coefficient

Magnetic Measurements

magnetic susceptibility
hysteresis

Crystallographic

lattice structure
crystallinity (degree of)

Optical Measurements

infrared absorption
visible light absorption
index of refraction
opacity
color

Mechanical Measurements

hardness
ductility
yield strength
creep
impact strength
elastic constants

Microscopic Studies

transmission electron
microscopy
replica electron
microscopy

gram-roentgen Amount of energy absorbed by one gram of air exposed to a dose of 1 roentgen (~ 84 ergs/g).

Radiation Ergs/cm²-sec.
Intensity

Rad Absorbed dose of 100 ergs/g (6.25×10^{13} eV/g).

1.3 PARTICLE-COLLISIONS

Collisions between primary radiation particles and the atoms in matter are of three main types: excitation collisions, ionization collisions and elastic collisions. In an excitation collision an atomic or molecular electron is raised to a higher energy level but still retained in the parent atom or molecule. In an ionization collision at least one of the collision partners becomes ionized and the struck atom is not displaced from its normal position as a direct consequence of the collision. The products of collision are an ejected electron and an ionized atom. In an elastic collision a relatively large amount of kinetic energy is transferred to the struck atom from the primary radiation particle and it is often knocked out of its normal position. An atom knocked out of place by a primary radiation particle is called a primary knock-on atom (PKA). Energetic PKA proceed to displace other atoms called secondary knock-on atoms (SKA); SKA produce tertiary knock-on atoms, etc. (See Figure 1.1). The term knock-on is a general term used to denote any energetic displaced atom, whether it be a PKA or an atom displaced by PKA, SKA, etc. The entire set of atomic collision initiated by a single PKA is called a PKA collision cascade. The radiation damage problem is often divided into two parts: (1) production of PKA, and (2) production of knock-on atoms in PKA cascades.

1.4 TYPES OF MATERIAL

In radiation effects work crystalline solids are usually classified as being:

1. Metallic
2. Ionic
3. Covalent
4. Molecular

depending upon the predominant type of bonding or bond holding their basic structural units together. The structural unit and a typical material associated with each bond type are:

<u>Bond</u>	<u>Basic Unit</u>	<u>Example</u>
Metallic	atom	iron
Ionic	atom	rock salt
Covalent	atom	silicon
Molecular	polymer molecule	polyethylene

UNCLASSIFIED

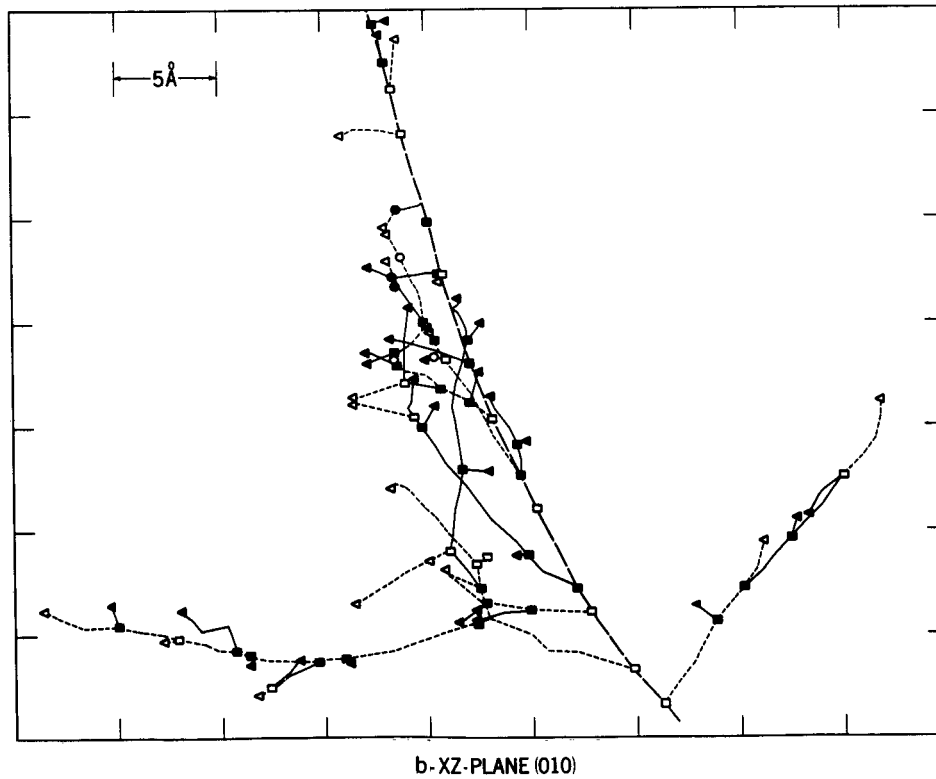
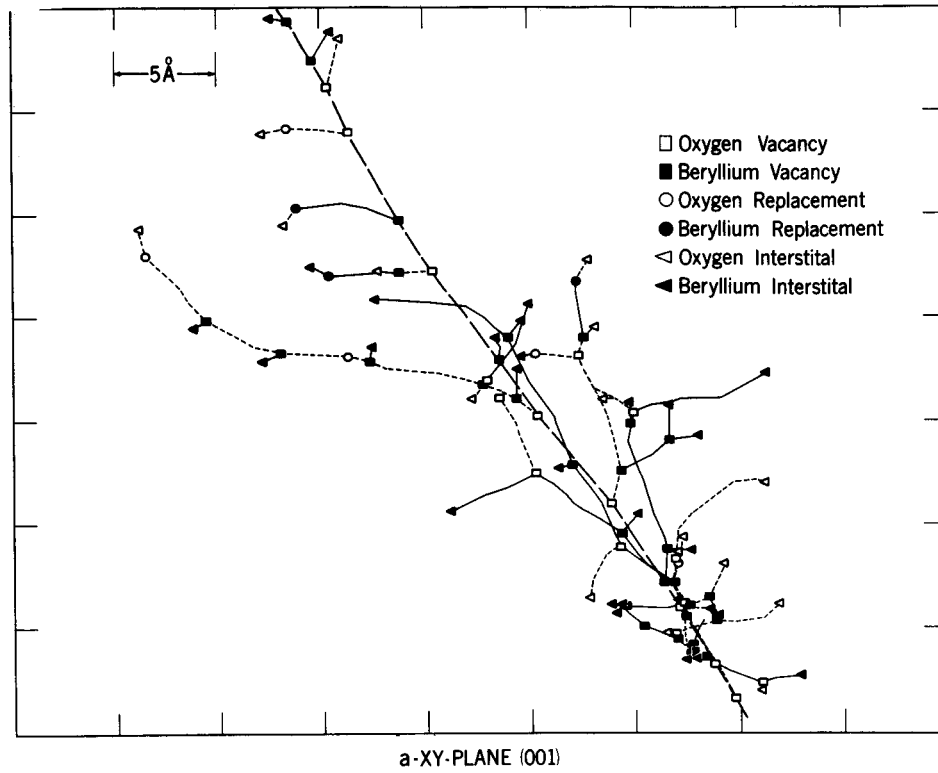


Fig. 1.1—Elastic collision cascade in BeO caused by a 5 kev iodine ion

UNCLASSIFIED

1.4.1 Metals

The basic type of radiation damage produced in metals is the displacement of atoms from normal positions in the metal lattice structure. This damage is produced mostly by elastic atom-atom collisions in the metal. Ionization events don't affect metals because there is a sufficient number of mobile electrons in a metal to immediately correct ionization effects.

1.4.2 Ionic Crystals

Both ionization and displacement damage occur in ionic crystals.

1.4.3 Covalent Crystals

As in metals, the major primary radiation effect is the displacement of atoms.

1.4.4 Molecular Crystals

These crystals are loosely bound. Because of this, nearly all conceivable types of radiation effects can occur. Radiation effects, particularly secondary effects, are very complicated in molecular crystals. Chemical considerations are important in this regard.

1.5 GENERAL EFFECTS

Figure 1.2 gives a fairly complete idea of specific ways materials are affected by radiation.

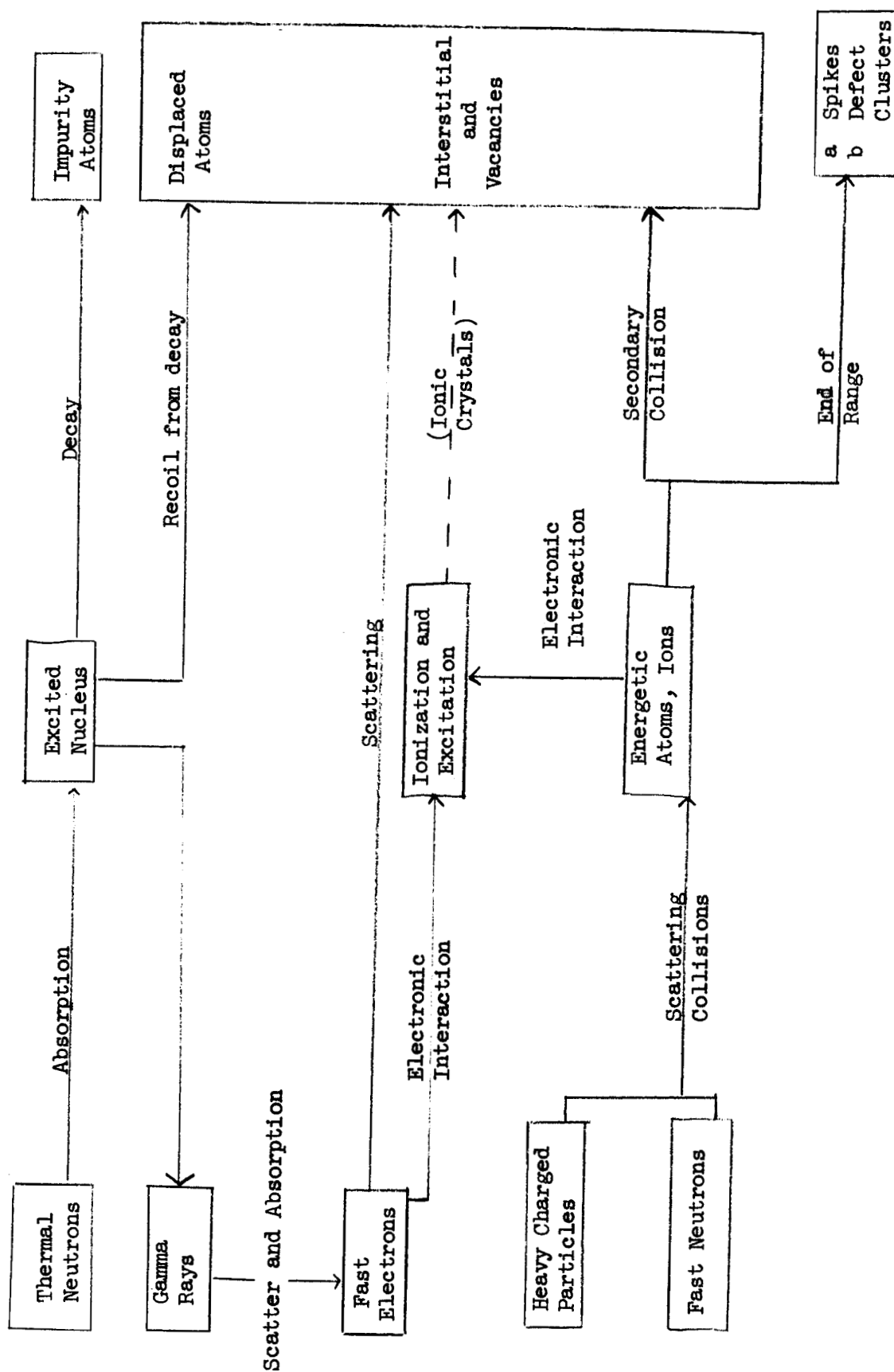


Fig. 1.2 Nature of Radiation Damage

(D.G. Billington, Nuc. Sept. 1960 p. 64)

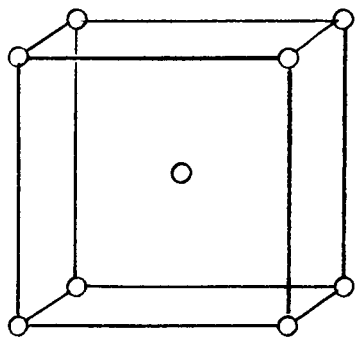
2. CRYSTALLINE SOLIDS

2.1 GENERAL CHARACTERISTICS

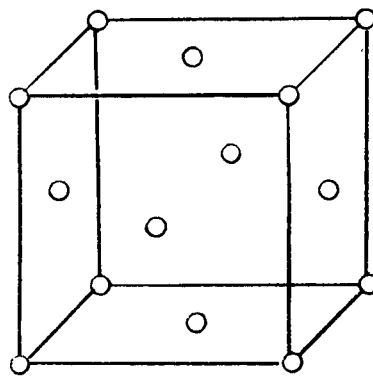
Metals, ionic crystals and covalent crystals are solids wherein atoms are positioned in a geometrically regular manner. Three common and elementary lattice structures, as they are called, are shown in Figure 2.1. The abbreviations bcc, fcc and hcp are used to designate body-centered cubic, face-center cubic and hexagonal close-packed structures, respectively. The rock salt and cesium chloride structures are also shown in Figure 2.1. The existence of this regular crystal structure gives crystals directional characteristics in that they shear on planes in which the atoms are most densely packed, atoms can be more easily displaced in some directions than others, and electrical properties are different for different directions. Also, the regular crystal structure provides electron energy bands. That is to say, electrons can have only those energies which fall into definite intervals called energy bands. These allowed energy bands arise from the way moving electrons are reflected and transmitted by the regularly arranged atoms in the crystal. The theory of this process is very much like that for electrical filters which allow only certain alternating current frequencies to pass and block the passage of all other frequencies. The principal electron energy bands of interest in radiation damage and effects work are (1) the valence band, and (2) the conduction band. Figure 2.2 shows these bands schematically.

In some crystals (insulators), there are normally no electrons in the conduction band. This comes about because of the very definite way electrons are experimentally observed to arrange themselves in the various energy levels contained within allowed bands. If the number of electrons available is exactly equal to the number the valence band will hold, there are none left over for the conduction band and the crystal is an insulator. These circumstances are strictly true only for perfect crystals at 0°K. If defects and/or impurities are introduced by radiation damage, the state of affairs is changed because any disturbance of a perfect crystal introduces new allowed electron energy levels. These new levels may be in the forbidden gap, for example, and under proper circumstances (high temperature) change an insulator into a semi-conductor. We will discuss this in more detail when we talk about semi-conductors per se.

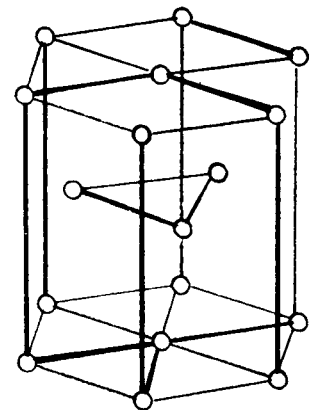
In metals, the number of available levels in the bands and the number of electrons available to fill them are such that there always exist electrons in the conduction band. Hence electron mobility in metals is greater than in any other material. This means that excitation and ionization "damage" in metals is immediately relaxed and the only damage of consequence is that of displaced atoms.



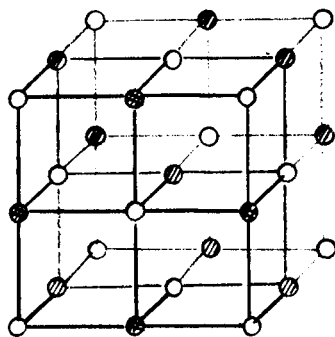
BODY-CENTERED
CUBIC LATTICE



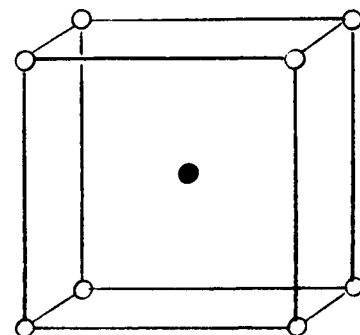
FACE-CENTERED
CUBIC LATTICE



CLOSE-PACKED
HEXAGONAL LATTICE



SODIUM CHLORIDE
LATTICE



CESIUM CHLORIDE
LATTICE

Fig. 2.1 - Common crystal structures

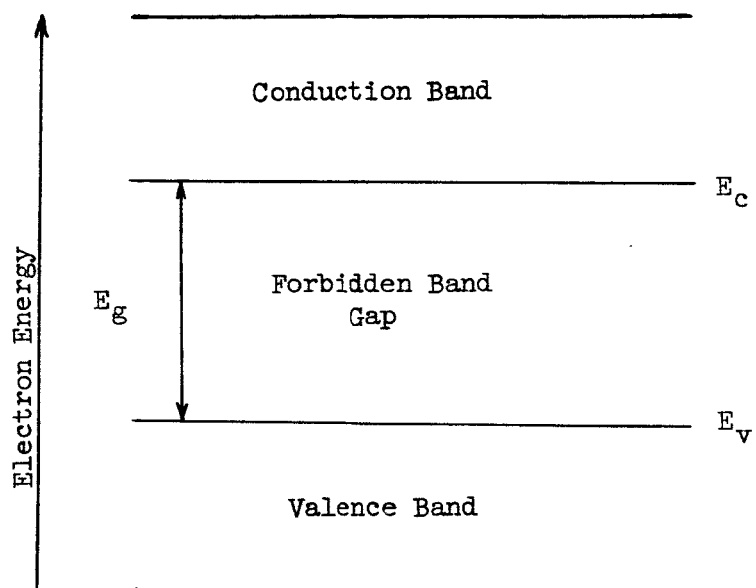


Fig. 2.2 Schematic representation of the electron energy band structure in crystalline solids.

In ionic crystals the metal atom loses an electron to the halogen atom. Hence the metal atoms are singly ionized (+) and the halogen atoms are singly charged ions (-). The electrostatic bond between these ion pairs holds the ionic crystal together.

We will first discuss radiation damage and effects in crystals and then turn to the more complicated radiation induced processes in organic materials and polymers.

3. THE ROLE OF TEMPERATURE (CRYSTALLINE SOLIDS)^{9, 10, 13}

In the first chapter of Frenkel's book, Kinetic Theory of Liquids, one can find a very nice description of thermal effects in solids. This chapter is entitled, "Real Crystals at Elevated Temperatures." Although radiation damage is not mentioned, this chapter is perhaps one of the best references one can read for the purpose of learning why irradiation temperature, and the entire temperature history of an irradiated material, are so important a factor in determining what radiation effects will occur.

The key idea is this. The velocity distribution of atoms in a solid is, at an elevated temperature T , the same in the solid, liquid and gaseous states. The possibility - more than that, the necessity - of an escape (evaporation) of atoms from their normal positions in a solid directly follows from this circumstance. The velocity component v_x of an atom with mass m in the x -direction has the distribution

$$f(v_x)dv_x = \sqrt{m/2\pi kT} \exp(-mv_x^2/2kT)dv_x \quad (2.1)$$

Similar distributions hold for the y - and z -directions and $f(v_x, v_y, v_z) = f(v_x) f(v_y) f(v_z)$. This is the famous Maxwell-Boltzmann distribution. If, for example, the thermal kinetic energy component $mv_x^2/2$ for the x -direction exceeds the magnitude of the potential energy U_0 associated with the atomic binding force along this direction, the atom will be "evaporated" from its normal lattice position and lodge itself in some interstice of the lattice. This leads to the production of a defect called either a "Frenkel pair" or a "Frenkel defect," composed of a vacant lattice site (called a vacancy) and an atom in a lattice interstice (called an interstitial atom). Figure 3.1 illustrates the Frenkel defect concept in two dimensions. Frenkel pairs exist in all crystals at an absolute temperature $T > 0$ and the number of Frenkel pairs existing per unit volume at a temperature T is

$$n_{\text{thermal}} = C_F \sqrt{NN'} \exp(-W/2kT) \quad (2.2)$$

where

$$C_F \approx 100$$

$$N = \text{number of lattice points per cm}^3$$

$$N' = \text{number of interstitial positions per cm}^3$$

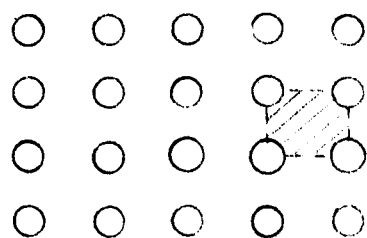
$$W = \text{work required to displace an atom}$$

$$T = \text{absolute temperature (}^\circ\text{K)}$$

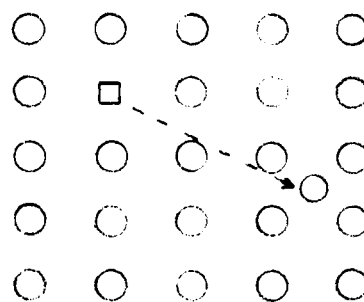
$$k = 1.38 \times 10^{-16} \text{ ergs/atom-}^\circ\text{K}$$

$$= 8.62 \times 10^{-5} \text{ eV/atom-}^\circ\text{K}$$

Equation 2.2 gives the equilibrium concentration of Frenkel pairs produced by thermal energy alone. Irradiation also produces Frenkel pairs by transferring sufficient energy to atoms to displace them. The total number of Frenkel pairs in an irradiated specimen is given by



(a) Perfect crystal at $T_0 = 0$. Circles denote atoms in normal lattice sites. The hatched region in a lattice interstice.



(b) Thermally produced Frenkel defect at a temperature $T > 0$. □ denotes a vacancy.

Fig. 3.1 - Frenkel defect

$$n_{\text{total}} = n_{\text{Thermal}} + n_{\text{Radiation}} \quad (2.3)$$

n_{total} , being the number measured.

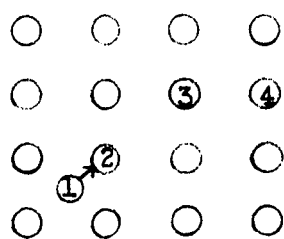
Atomic diffusion in crystals proceeds either via the movement of interstitial atoms or the movement of atoms into vacancies, i.e., the positional interchange of a vacancy with an immediately neighboring atom (See Figures 3.2 and 3.3). Once a vacancy and an interstitial atom are produced, less energy is required for the movement of the interstitial atom than for the movement of the vacancy. The minimum energy required for defect movement is called the migration energy E_m^m . Usually, in metals, the migration energy E_m^i for interstitial movement is considerably less than the vacancy migration energy E_m^v and low temperature irradiation effects, depending upon defect movement, are almost totally the result of interstitial atom migration, vacancy motion being severely inhibited. At high temperatures the difference between interstitial atom and vacancy mobility decreases and both defects migrate freely.

Because radiation damage is a complex process most competent investigators make at least four different types of physical property measurements, simultaneously, as a function of temperature and radiation exposure, and, if possible, they make transmission electron microscope pictures of the irradiated specimen material. By using cross correlation of the changes in several physical properties and these electron microscope pictures, a rather good description of radiation damage can be made. It is nearly always impossible, however, to make any sense out of the data when just one type of radiation effect is measured.

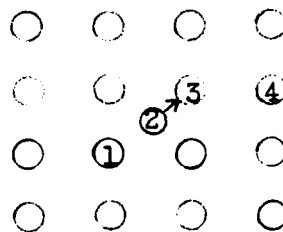
At this point we will jump to an assertion which, logically, should be made at the end of this lecture, following an orderly presentation of the supporting evidence. The assertion is as follows: The types of radiation effects produced by a given type of radiation in a given specimen are importantly dependent on environmental circumstances. All other environmental factors being held constant, the temperature at which the sample is irradiated and whether the radiation effect measurements are made during or after irradiation largely determine what type radiation effects will be detected and the magnitude of these different effects. Hence there is a minimum number of four major classes of temperature-irradiation conditions under which radiation effects measurements should be made to bracket the range of possible radiation effects an engineer should account for in hardware design. These are listed in Table 3.1.

TABLE 3.1

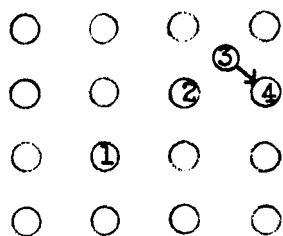
<u>Specimen Temperature</u>	<u>Effect Measured</u>
Low temperature	During irradiation
Low temperature	After irradiation
High temperature	During irradiation
High temperature	After irradiation



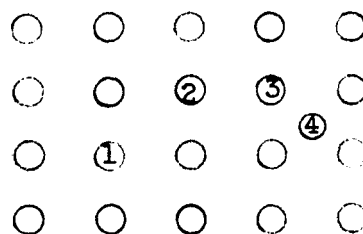
(a)



(b)



(c)



(d)

Fig. 3.2 - Interstitial atom movement via the interstitialcy mechanism

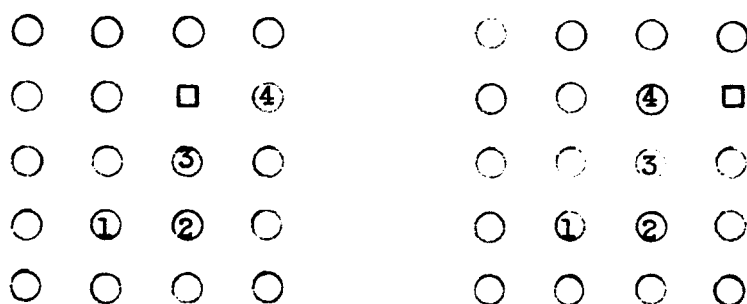
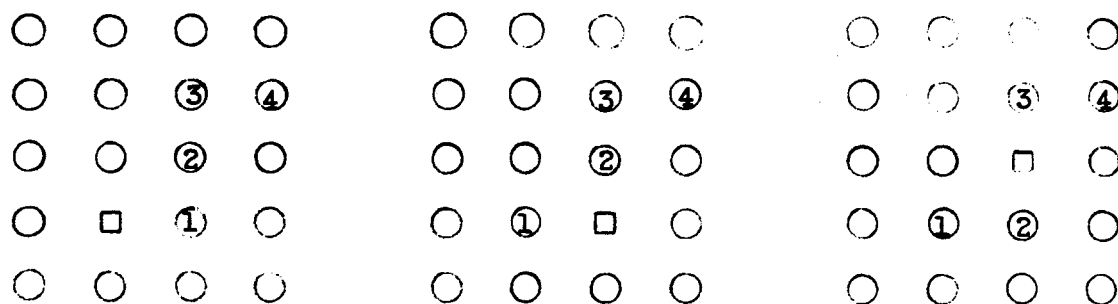


Fig. 3.3 - Vacancy movement via positional exchange

For example, the creep rate of iron at a high temperature T during irradiation in a reactor is significantly smaller than the creep rate one observes in the same specimen after the irradiation has been "turned off" and the temperature maintained at the same level T .

In summary, temperature plays a fundamental role in radiation effects studies because every reaction process has an activation energy E_a and the rate at which a reaction will proceed is proportional to the number $\exp [-E_a/kT]$. At any given temperature the reactions which are important (most probable) are determined by the magnitudes of their activation energies.

4. DISLOCATIONS^{14, 15, 16}

If you want to move a rug a short distance, the easiest way is to form a wrinkle in the rug and then move the wrinkle as shown in Figure 4.1. The edge b is displaced a distance Δb , given in Figure 4.1, where d is the diameter of the wrinkle. Deformation of crystals proceeds in a similar manner, the local distortion by which it proceeds being called a dislocation. Figure 4.2 is a picture of an edge dislocation. It turns out that when dislocations cross each other they tend to lock together and deformation is impeded. Dislocation motion is also impeded by the strain (stress) localized about impurity atoms and interstitial atoms. Finally, the collapse of vacancy clusters and interstitial clusters leads to the formation of little dislocation rings. These rings affect the movement of other dislocations and the diffusion of vacancies and interstitial atoms. It is the interaction between dislocations and radiation induced defects that causes the mechanical strength of crystalline solids to be affected by irradiation.

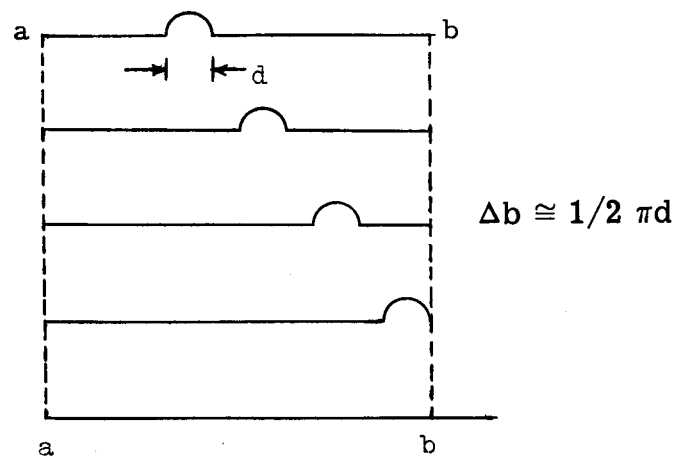
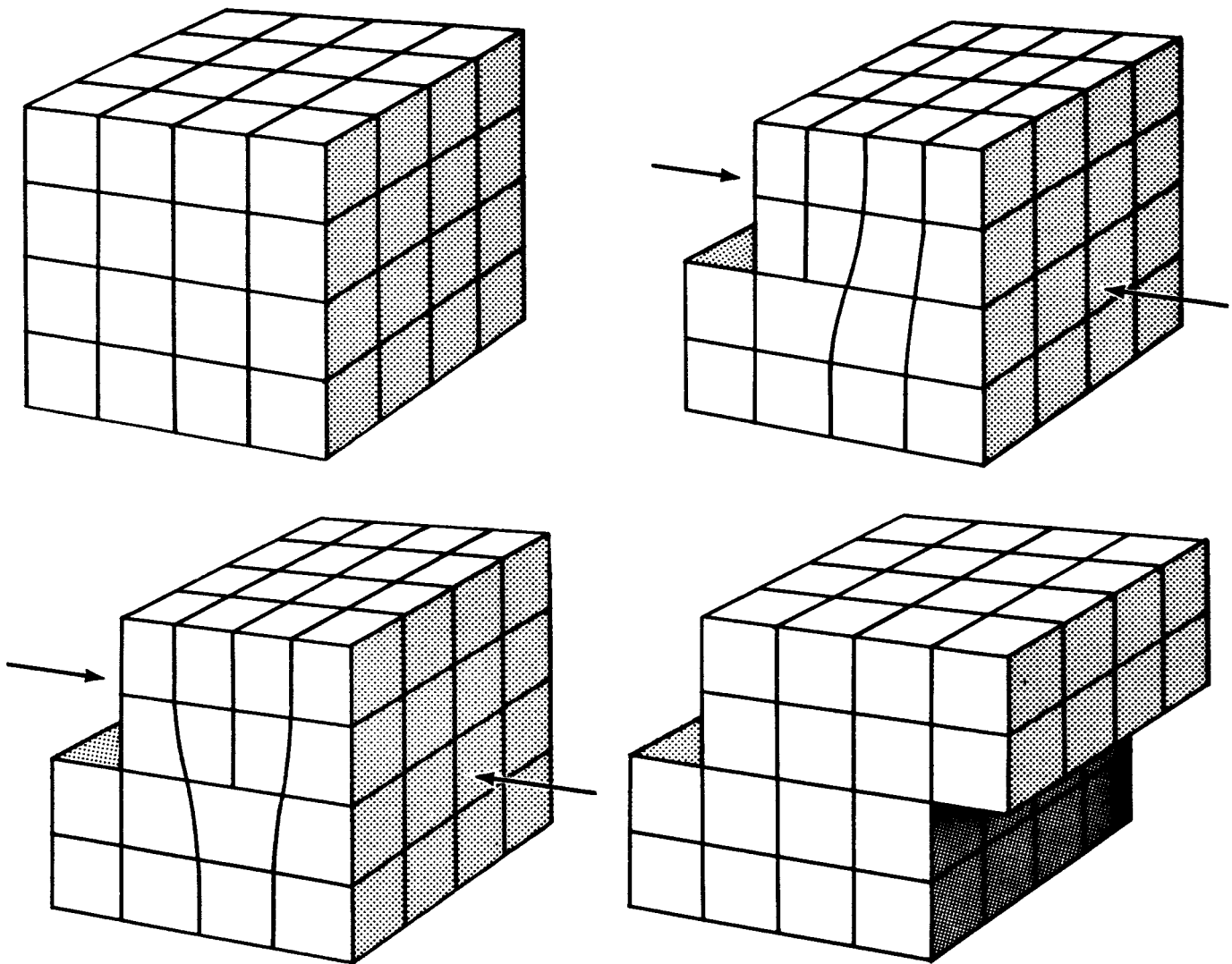


Fig. 4.1 Rug wrinkle model for a dislocation.



EDGE DISLOCATION is diagramed. At upper left is a simplified drawing of a perfect crystal like the one at the top of the page. Under stress part of the crystal is squeezed one atomic spacing (upper right). An "extra" plane of atoms appears; the region at its base is an edge dislocation. The dislocation moves across the crystal (lower drawings), deforming it in a series of discrete steps.

Fig. 4. 2

5. RADIATION DAMAGE IN CRYSTALS ⁶⁻¹¹

5.1 METALS

The interest in irradiation effects in metals arises directly from their use in nuclear reactors. Most of the irradiation effects study has therefore been that associated with neutron irradiation damage. Most of the emphasis has been placed upon mechanical and electrical effects. The particular irradiation effects observed in metals depend sensitively upon the temperature during irradiation and the thermal history subsequent to irradiation as well as upon the radiation dose.

Volume Change

The volume increase per vacancy-interstitial pair is believed to be 1.5 the atomic volume. This is the net effect of expansion due to the large pressure exerted by an interstitial and the shrinkage about a vacancy.

Elastic Properties

In principle, the presence of imperfections can change the elastic properties of a metal because they change the average lattice constant (distance between atoms). If the effect of interstitials outweighs that of vacancies, Young's modulus should be increased by the presence of vacancies and interstitials. Apparently the effect in a given metal depends upon its structure and the temperature. The effects observed are small.

Electrical Resistivity

Radiation changes the electrical resistivity a measurable amount for all metals. Because of this, electrical resistivity measurements are a standard method for detecting radiation damage and for "measuring" the annealing of radiation induced defects. The change in resistivity per atomic percent of defects is of the order of 0.7-1 micro-ohm cm.

Mechanical Properties

The interaction of dislocations with point defects strengthens and hardens a metal. During irradiation vacancy clusters and interstitial clusters form and collapse to form dislocation rings. These rings can be effective in further impeding "normal" dislocation movement.

5.2 SEMI-CONDUCTORS

A semi-conductor is a crystal wherein the electronic conductivity is greater than $10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$ and increases with temperature as $e^{-b/T}$. Semi-conductors are extremely sensitive to radiation damage. The gross changes induced in diamond- or zinc-blend structure semi-conductors are summarized in Table 5.3. Discounting effects of electron

TABLE 5.1

CHANGES IN TENSILE PROPERTIES OF ALLOY STEELS*

Dose (nvt; > 1 Mev)	Yield Strength (10^3 psi)	Ultimate Strength (10^3 psi)	Total elong. (%)	Uniform elong. (%)
8.5% Ni				
0	91.8	119	29.5	21.5
1.7×10^{19}	138	148	18	11
1×10^{20}	183	184	5.5	2
Carilloy T-1				
0	120	129	14	8
1.7×10^{19}	170	171	4.5	0.5
1×10^{20}	186	187	3.7	0.3

*Strain rate = 0.5 in./min.; irradiation temperature = 205°F.

TABLE 5.2

HOW 5×10^{19} NVT (EPITHERMAL) CHANGES MECHANICAL
PROPERTIES OF VARIOUS METALS

Testing	Yield strength (10^3 psi)		Ultimate strength (10^3 psi)		Elongation (%)	
Temp.						
(°F)	Before	After	Before	After	Before	After
Zirconium (cold-worked)						
78	107	106	124	124	3.5	4.2
194	103	96	115	115	2.7	3.4
320	92	90	101	106	1.9	2.9
390	87	82	91	93	2.1	2.7
Molybdenum						
78	93.7	99.4	99.8	104.3	23.6	22
194	80.3	93.3	90.5	93.5	23.8	18.4
390	70.4	85.5	74.6	85.9	2.8	5.8
Tungsten						
390	148	131	173	173	2.4	4.2
Nickel						
-320	38	90.8	88	105	32	15
-108	38	75	70	78	41	24
78	36	62	59	63	34	23
390	34	54	51	59	27	19

TABLE 5.3

EFFECT OF IRRADIATION ON THE ELECTRICAL PROPERTIES OF
CERTAIN SEMICONDUCTORS

Material	Response to Irradiation	References
n-type Ge	converted to p-type	
p-type Ge	approaches a limiting hole concentration ($7 \times 10^{16} \text{ cm}^{-3}$)	
n & p-type Si	carrier concentrations approach intrinsic value	
n-type InSb	approaches a limiting electron concentra- tion ($4 \times 10^{16} \text{ cm}^{-3}$)	
p-type InSb	converted to n-type	
n-type GaSb	converted to p-type	
p-type GaSb	approaches a limiting hole concentration ($\sim 10^{16} \text{ cm}^{-3}$)	
n-type AlSb	approaches a limiting electron concentra- tion	
p-type AlSb	converted to n-type	
n-type InAs	electron concentration appears to increase indefinitely	
p-type InAs	converted to n-type	
n-type InP	electron concentration decreases, no evidence of conversion	
p-type CdTe	converts to n-type	

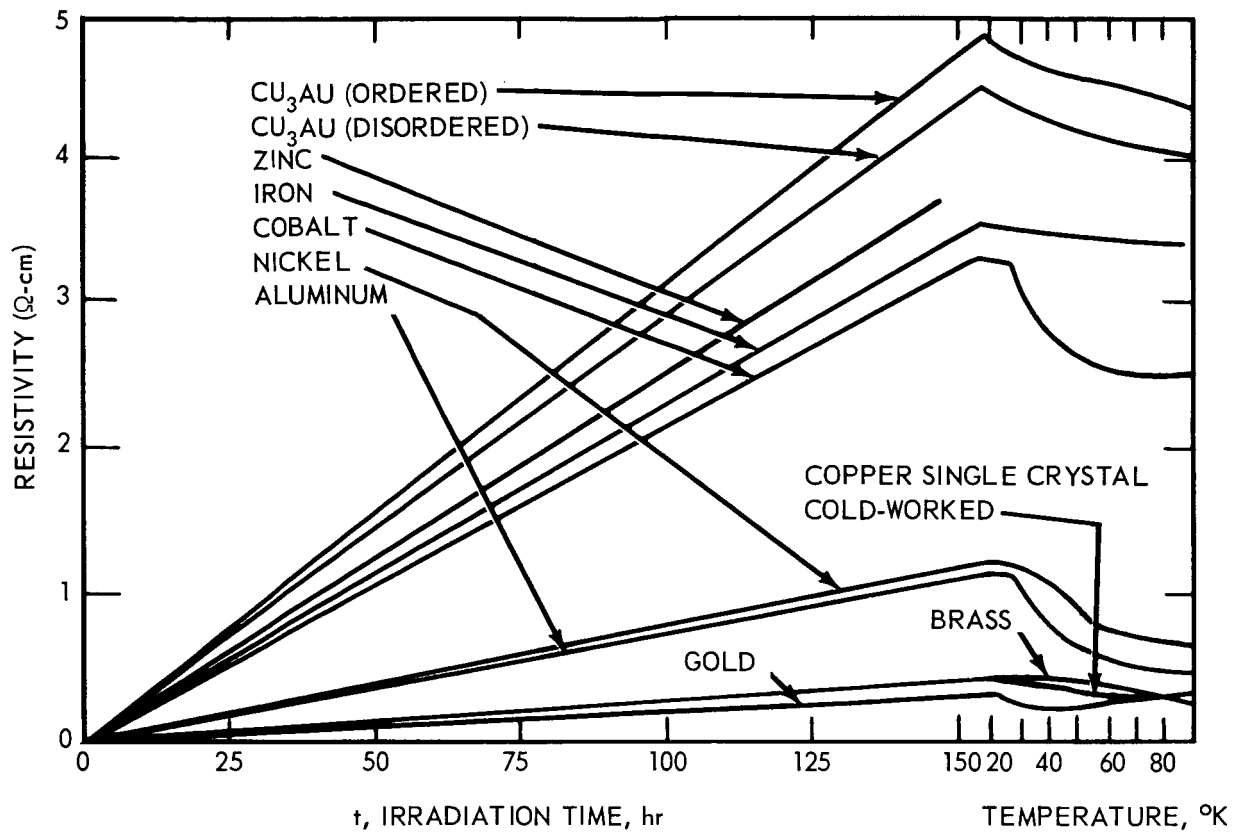


Fig. 5.1 - Electrical resistivity

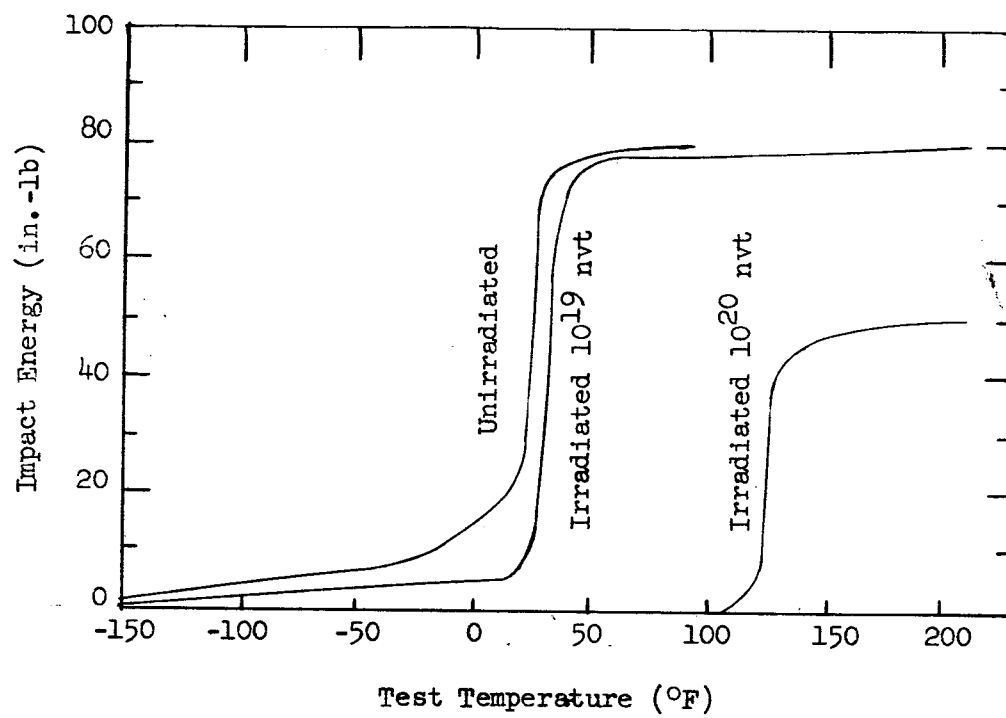


Fig. 5.2 Brittle Fracture

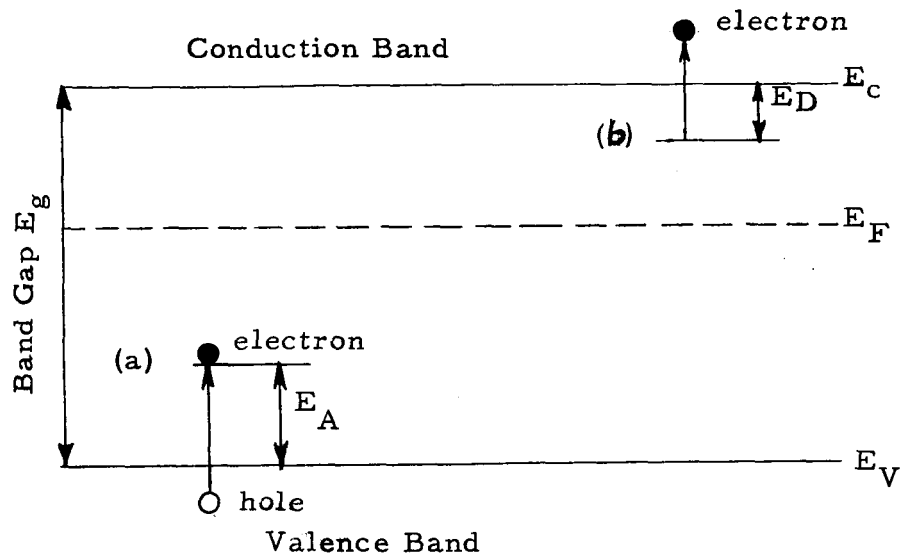


Fig. 5.3 - Semi-conductor energy diagram. Electrons are thermally excited from donor level E_D into the conduction band to provide electron conduction, and from the valence band up to acceptor level E_A to provide a hole in the valence band. In this case the semi-conductor is called an extrinsic semi-conductor. If E_g is sufficiently small that electrons can be excited thermally from the valence band into the conduction band one has an intrinsic semi-conductor.

irradiation at low temperatures on InSb, only Ge and GaSb are converted from n-type to p-type. In silicon, defects appear to be equally effective as acceptors and donors and hence produce an intrinsic material regardless of whether silicon was n-type or p-type before irradiation. All of the remaining Group III-V compounds are converted from p-type to n-type, indicating that the level shifts are in the direction of the conduction band.

By virtue of either temperature of impurity and/or defect content, the charge carrier concentration in semi-conductors varies markedly. This is not true for metals wherein the concentration of charge carriers is fixed and is the same order of magnitude as the density of atoms in a crystal. In intrinsic semi-conductors, the concentration of electrons, n , in the conduction band is equal to the concentration of holes, p , in the valence band. These concentrations are produced by thermal ionization of atoms (valence bands) or ions in the crystal.

$$n_i^2 = n \cdot p = N_c N_v e^{-E_g/kT} \quad (5.1)$$

where

n_i = intrinsic concentration

E_g = width of forbidden gap between the valence and conduction bands

$N_c = 2g_c (2\pi m_n kT/h^2)^{3/2}$ is the effective concentration of available electronic states in the conduction band, and

$$N_v = 2g_v (2\pi m_p kT/h^2)^{3/2} \quad (5.2)$$

is the effective density of available states in the valence band. m_n and m_p are the electron and hole effective masses, respectively, and the g 's are statistical weight factors.

The carrier product $n \cdot p$ determines the minority carrier concentration in extrinsic semi-conductors.

The type and concentration of charge carriers in an extrinsic semi-conductor is determined by

1. structural imperfections
2. chemical impurities
3. lattice defects

These form localized (in space) electronic states in the gap which may ionize thermally as donors (or acceptors) to yield electrons (or holes). If there are N_D donors

$$\frac{n^2}{N_D - n} = N_c e^{-E_D/kT} \quad (5.3)$$

E_D is the donor ionization energy. Since, however, acceptors and donors are simultaneously present, they tend to compensate (neutralize) each other. When this occurs it is the net donor or acceptor concentration which is important and one has

$$\begin{aligned} n &= N_C \exp (E_F - E_C)/kT & E_C &= \text{bottom of conduction band} \\ p &= N_V \exp (E_V - E_F)/kT & E_V &= \text{top of valence band} \end{aligned} \quad (5.4)$$

E_F is the very important "Fermi Energy." E_F is the energy level which has a 50 percent chance of being occupied by an electron. The concentration of electrons with energies above E_F is equal to the concentration of holes with energies below E_F . If E_F lies above the middle of the gap, the material is an n-type semi-conductor; if E_F lies below the middle of the gap, the material is a p-type semi-conductor.

The electrical conductivity of an intrinsic semi-conductor is

$$\sigma = e(U_n n + U_p p) \quad U = \text{mobility} \quad (5.5)$$

When radiation disturbs the electron-hole concentration, a finite time is required to restore equilibrium. The lifetime of excess electron-hole pairs or, more commonly, the lifetime τ of minority carriers is an excellent probe for use in studying radiation damage in semi-conductors. It also represents the time for transient currents to relax in pulse-irradiated transistor circuits.

$$\tau = \frac{\frac{1}{C_p}(n_0 + n_1) + \frac{1}{C_n}(p_0 + p_1)}{n_0 + p_0} \quad (5.6)$$

n_0, p_0 original concentrations

$$n_1 = N_C e^{-(E_C - E_r)/kT}$$

$$p_1 = N_V e^{(E_V - E_r)/kT}$$

$$C_p = N_r \sigma_p v_p$$

$$C_n = N_r \sigma_n v_n$$

Normally the direct combination of electrons and holes is (highly) forbidden. Excess electron-hole pairs therefore annihilate at localized electronic states furnished by defects where the rules for recombination are very relaxed. These are called recombination centers. N_r is their population. E_r is the energy level associated with the recombination center. v is velocity and σ is a capture cross section. τ is of the order of microseconds, and increases with temperature. For neutron irradiated Ge, τ lies between 15-100 μ sec (2×10^{12} nvt).

Electronic Circuits

When an electronic circuit is subjected to radiation pulses, two types of transient effects arise: a primary transient accompanying the direct radiation interaction, and a secondary transient arising the distortion of signals during the time the radiation damage relaxes. The main cause for changes in circuit characteristics is induced electrical leakage. This has the effect of introducing extra (parallel) loops in the circuit. Clearly low impedance circuits are thus less affected than high impedance circuits. The fundamental damage mechanisms remain as (1) displaced atoms (2) ionization. Coaxial cables are subject to internal leakage which varies non-linearly with applied potential.

6. ORGANIC MATERIALS^{4, 5}6.1 GENERAL CONSIDERATIONS

Carbon atoms tend to form long chain molecules which give rise to many organic compounds (over 10^6 of these have been definitely characterized as to composition, structure and properties -- several million more exist which have not yet been characterized). The backbone of all organic compounds is a skeleton of carbon atoms linked in simple or branched chains. Carbon usually has four bonds which permit linkage with four other atoms. Covalent bonding of carbon with another atom, consists of a sharing of two electrons between carbon and this atom. If each atom supplies an electron in the covalent bond, the bond is termed a normal covalent bond. When one atom supplies both electrons the bond is called a coordinate covalent bond.

An organic material (compound) is one containing carbon combined with one or more of the following elements:

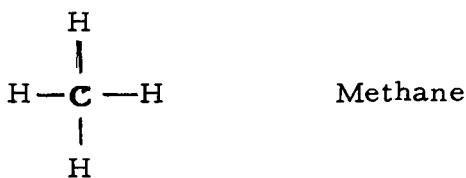
hydrogen	sulfur	bromine
oxygen	fluorine	iodine
nitrogen	chlorine	phosphorous

Table 6.1 gives the normal covalent bond energies for carbon linked with other atoms.

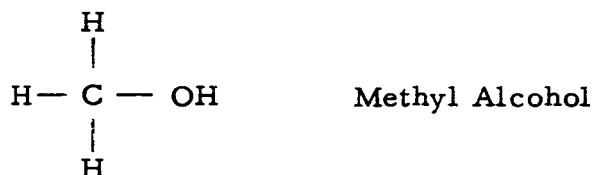
TABLE 6.1

<u>Bond</u>	<u>Bond Energy</u>	
	<u>kcal/mole</u>	<u>eV</u>
C-F	93.2	4.05
C-Cl	69.6	3.04
C-Br	58	2.5
C-I	43	1.9
C-H	90.8	3.94
C-C	64.5	2.80

An important structural concept in organic chemistry is that of the radical and the group. A radical is an assembly of atoms which acts as a single atom, in molecular structure, and tends to retain its identity throughout a series of reactions. When this assembly is unattached in the free state with an unpaired electron, it is called a free radical. When attached in a molecule it is called a group. As an example, consider methane,



and methyl alcohol,

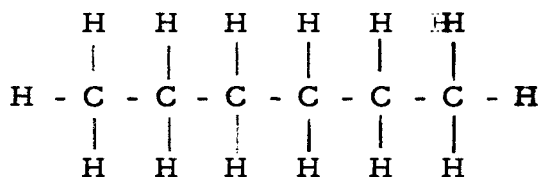


Methyl alcohol is formed by substituting the OH radical for a hydrogen (radical) H in methane. In the unattached free state either CH_3^\cdot and OH^\cdot are called free radicals; when combined to form methyl alcohol they are referred to as groups. An irradiated organic material tends to break up into free radicals.

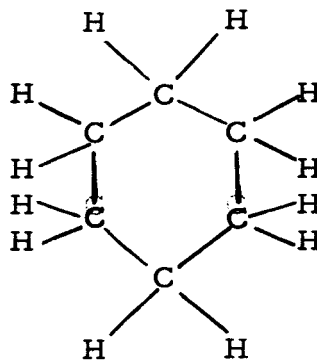
6.2 HYDROCARBONS

The hydrocarbons, made up of carbon and hydrogen make up an enormous number of organics. Carbon atoms tend to form shared electron (covalent) bonds with other atoms and other carbon atoms. Carbon tends to occupy a position at the center of a tetrahedron with 4 covalent bonds pointing out to the points of the tetrahedron. Each bond consists of 2 electrons being shared with the associated atom.

Organic compounds are classified as chain compounds (aliphatic) or cyclic compounds,

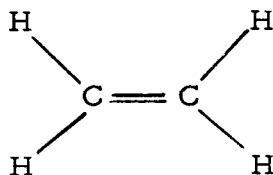


Hexane (aliphatic)

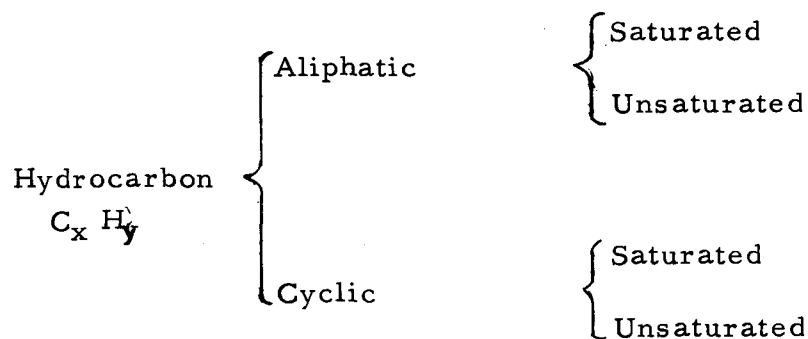


Cyclohexane (cyclic)

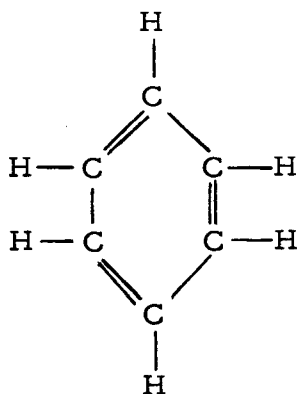
In a saturated compound, carbon atoms are joined by a single bond; in unsaturated compounds by more than one bond. Hexane, for example, is saturated but ethylene is unsaturated as it contains a double bond.



It is important to remember these circumstances because saturated organics are usually more radiation-resistant than unsaturated organics; i.e., the saturated bond is the stronger bond. Aromatics are an exception to this rule.

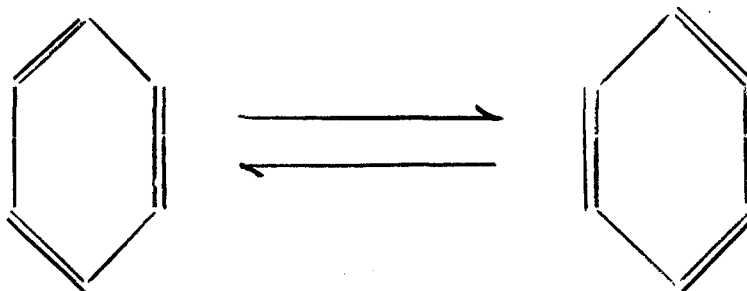


Aromatic hydrocarbons are those based on the benzene ring,



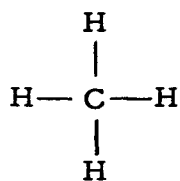
Benzene

The double bonds between carbon atoms "resonate" by switching positions

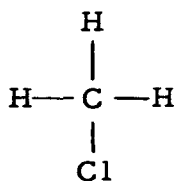


This property enables an aromatic unit to withstand relatively more radiation than other structures. This circumstance leads to an exception to the statement made immediately above that unsaturated bonds are undesirable.

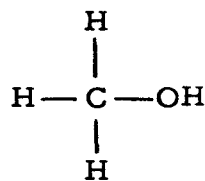
Many compounds can be considered as derivatives of hydrocarbons because they (theoretically) come about by substituting another element or groups of elements for hydrogen in the corresponding hydrocarbon, i.e., one containing the same number of carbon atoms. The following diagram illustrates derivatives of methane.



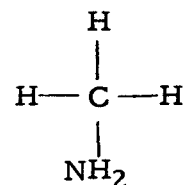
Methane



Methyl Chloride



Methyl Alcohol

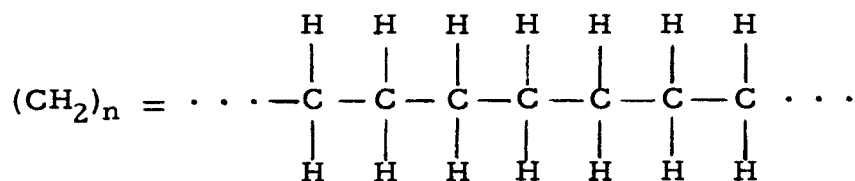


Methyl Amine

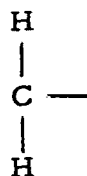
In unsaturated compounds other atoms, groups or radicals can be introduced by mere addition. In saturated compounds other atoms, groups or radicals can be introduced only by the replacement of atoms (usually hydrogen) in the original saturated molecule.

6.3 POLYMERS

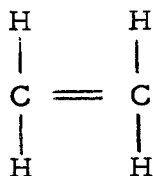
High polymers result when a chain or network of identical groups is formed. Polymers are macromolecules with molecular weights of the order of $10^3 - 10^6$. In this special organic molecule the basic structural unit is called a mer, the weight of a mer being the mer weight. A monomer is simplest original chemical unit used to form polymers. As an example, polyethylene is a linear polymer with the structure,



The mer of polyethylene is



with mer weight $2 + 12 = 14$. The monomer is the unsaturated ethylene molecule,



During polymerization to polyethylene the double bond $\text{C} = \text{C}$ goes over into $\text{C} - \text{C} -$. The number of mers in a polymer molecule is called the degree of polymerization (D.P. or n). The molecular weight of a polymer molecule is $(\text{D.P.}) \times (\text{mer weight})$. A collection of polymers forming a liquid or solid polymer material is characterized by a distribution of D.P. There is no single D.P. for a polymer material.

The average degree of polymerization DP or n is often used to specify the molecular weight of a polymer material. Polymers do not have well defined physical properties. They differ from batch to batch.

Linear polymers are either random or ordered assemblies of polymer molecules. Schematically a linear polymer is as shown in Figure 6.2.

Space polymers or cross linked polymers contain bonds running transversely from one molecule to another. A space polymer material is one big molecule. The degree of cross linking is signified, in a sense, by stating the cross link molecular weight M_c of all atoms involved in cross linking.

6.4 PHYSICAL PROPERTIES OF POLYMERS

In contrast with low molecular weight materials, polymers exhibit great variability and temperature dependence of their macroscopic properties. The latter are determined primarily by the properties of the individual molecules, the molecular order, and the mobility of the chain segments.

Table 6.2 lists some of the macroscopic properties of polymer systems along with their most important relevant structural molecular parameters. Before a linear polymer system exhibits a measurable degree of mechanical strength, it must attain a certain minimum degree of polymerization which varies inversely with specific molar cohesion. As examples we may mention polyamides which require a minimum D.P. of 40 since they have fairly large intermolecular forces, and polyhydrocarbons with a minimum D.P. of 80 since their intermolecular forces are lower. As soon as this minimum D.P. value is attained, the mechanical strength increases approximately proportional to the increase in D.P. until, at values of about 200-300, the slope of the curve becomes flatter. Both molecular orientation and crystallization, since they increase the intermolecular forces, will also increase the mechanical strength.

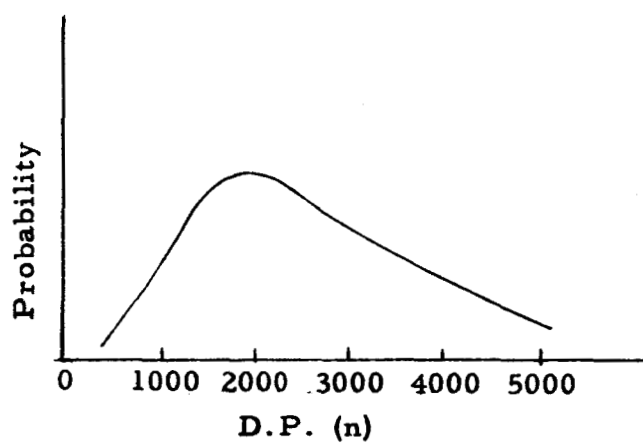
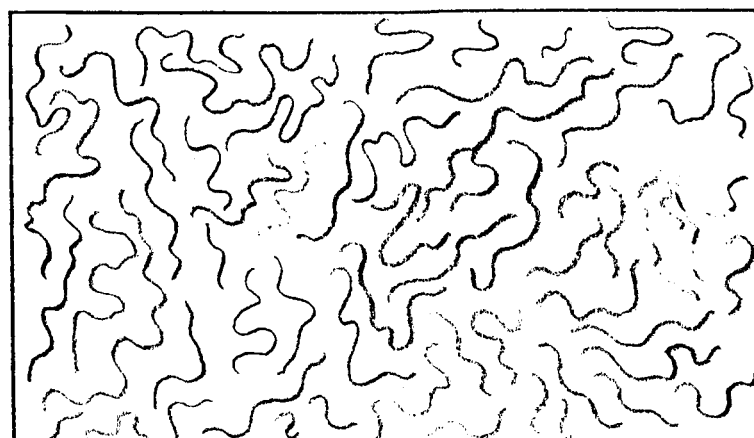
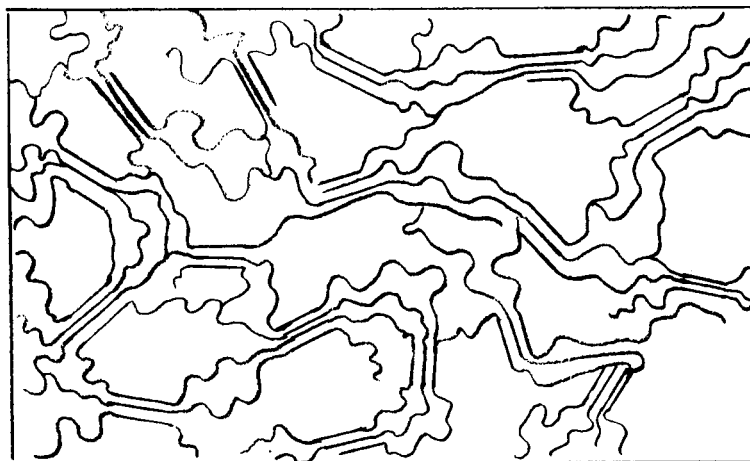


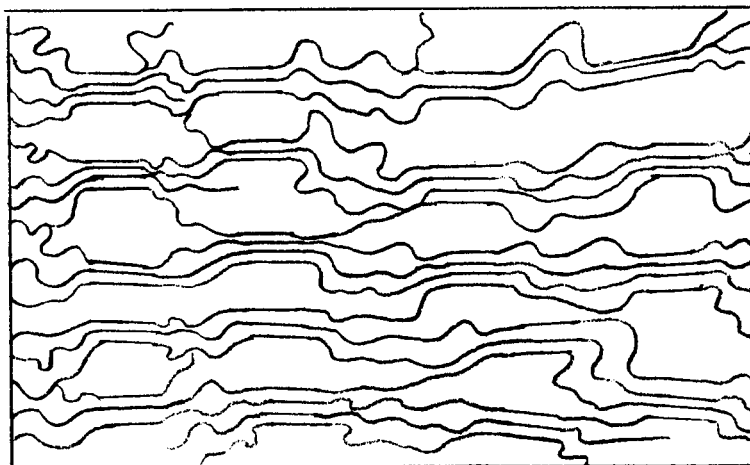
Fig. 6.1 Schematic representation of the degree of polymerization (D.P.) distribution in a high polymer specimen.



(a) RANDOM
CHAIN
DISTRIBUTION



(b) UNORIENTED
CRYSTALLINE
POLYMER



(c) ORIENTED
CRYSTALLINE
POLYMER

Fig. 6.2

TABLE 6.2

CORRELATION OF MACROSCOPIC PROPERTIES
WITH MOLECULAR PARAMETERS

Property	Structural Molecular Parameters
Mechanical strength	orientation; crystallinity; minimum chain length required; amorphous polymer require cross-links; fillers
Tensile strength	orientation; crystallinity; network formation
Tensile and torsional moduli dynamic modulus	orientation; crystallinity; branching
Stiffness	chain length distribution (presence of long chains favorable, crystallinity not too high) spherulite-free structure
Brittleness	high crystallinity; spherulite structure
Impact resistance	small amounts of very low molecular weight species are unfavorable
Folding endurance	crystallinity; orientation cross-linking
Plasticity	addition of plasticizing agents which increases the mobility of the polymer molecules
Deformability at higher temperature	chain length and branching
Cold drawing	crystalline fraction; cross-linking
Abrasion	spherulite structure favorable, small amounts of low molecular weight fractions unfavorable
Time-dependent properties creep elastic recovery tensile stress relaxation variable service conditions	intermolecular forces, crystallinity; type of cross-linkage; presence of plasticizer; molecular mobility

TABLE 6.2
(Cont.)

Property	Structural Molecular Parameters
Fatigue	small amounts of very low molecular weight fractions unfavorable
Melting point	chemical constitution; ratio of crystalline to amorphous structure, orientation
Glass transition temp.	chemical constitution; ratio of crystalline to amorphous structure; internal order; plasticizing agents
Solubility Swelling ability	chemical constitution, degree of crystallinity; chain length distribution; degree of branching
Water absorption	chemical constitution; degree of crystallinity; orientation
Translucency	morphological structure
Dielectric loss factor and dielectric constant	chemical constitution; degree of crystallinity; impurities, e.g., by traces of catalyst
Electric arc resistance	spherulite structure unfavorable

There is no simple correlation between molecular-weight distribution and physical properties, but generally it may be stated that the presence of small amounts of low-molecular weight fractions (with D.P. < 100 or 150) has a deleterious effect on most mechanical properties (e.g., tensile strength, folding endurance, etc.).

The factors affecting solubility can be gathered from empirical data. Favoring solubility are:

1. Chemical and structural similarity.
2. Similar polarity.
3. Similar internal pressures.

Solubility decreases with:

1. Increasing melting point of the solute.
2. Increasing molecular weight of solute.

Solubility is also significantly determined by molecular weight distribution. Solution takes place fairly rapidly with systems having molecular weights up to 5000. Above molecular weight 10000, polymer systems dissolve much more slowly.

Solution is preceded by an extended swelling process during which the individual segments of the molecule are solvated. Finally a highly viscous solution may be taken as evidence that the substance is a high polymer.

In many cases swelling is not followed by complete solution. Such limited swelling is due either to crystallinity or to cross-linking. In the latter case, the degree of swelling can furnish us information about the degree of cross-linking. Solubility properties are important in radiation work because some of the decomposition products split off by irradiation act as local solvents and soften the polymer.

7. RADIATION DAMAGE PROCESSES IN ORGANIC MATERIAL^{4, 5}

This is a long chapter because the number of damage possibilities involved is large. First we will touch on photochemical reactions as they are excellent prototypes for the type of secondary processes one finds in the general radiation damage process. Then at the risk of some repetition a description of the general process will be attempted.

7.1 PHOTOCHEMICAL REACTIONS

In photochemical reactions, it is useful to separate the reaction steps which constitute the total process into primary and secondary reactions. The primary reactions are those which the molecules undergo immediately after absorbing a photon. The secondary reactions are the terminal steps involving radicals or other products of the primary reaction. Very few reactions are simple reactions. The viewpoint that all reactions are the result of a combination of consecutive and simultaneous reaction steps must be kept in mind while studying the effects of all types of radiations on chemical compounds.

In order for molecules to react, they must be activated. Under ordinary conditions, only a small number of molecules (the number is determined by the Boltzmann distribution) can react. Raising the temperature increases the thermal agitation and therefore increases the rate of reaction. A 10°C rise in temperature doubles the reaction rate in many cases. In photochemical reactions, the energy of activation is provided by the energy of electronic excitation of the molecules which have absorbed photons. There are two paths of activation; some of the molecules are electronically excited whereas others are ionized. Both the excited molecules and the ions are capable of undergoing further reaction.

As a consequence of electronic excitation, the molecules may dissociate into radicals or may undergo a process of internal conversion, i.e., transfer of the excitation energy of the electronic system into vibrational energy of the constituents of the molecule. Thus, the molecule will vibrate and react chemically like a molecule at high temperature. These reactions may involve other molecules, or the original molecule may break up into radicals or stable molecules. The subsequent thermal reactions of these radicals and molecules determine the course of the over-all reaction. Ions similarly produce radicals or molecular products, either directly or as a result of recombination.

7.1.1 Excitation

In general, an excited molecule can lose its energy in different ways, among which are:

1. Predissociation
2. Collisions
3. Photon emission
4. Migrations (of little importance in organics)

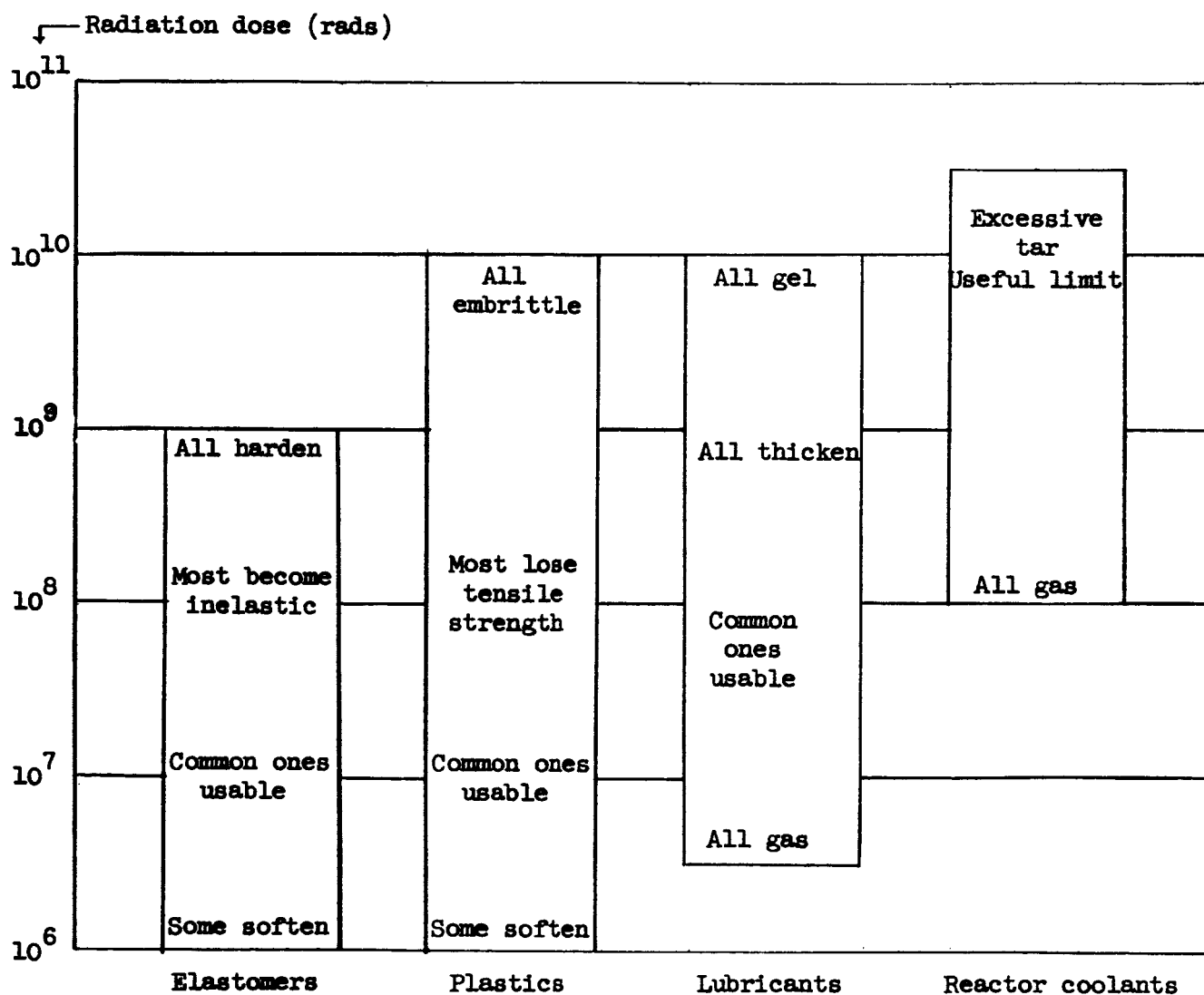
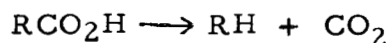


Fig. 7.1 - Sensitivity of organic materials to radiation

Predissociation

Whenever two different electronic states of a molecule have the same nuclear configuration and total energy, there is a finite probability that a molecule which is in one of these states will "cross over" into the other. As a result of this process, a molecule in an excited state in which it does not have enough vibrational energy to dissociate, may after a lapse of time cross over into a second excited state in which it is unstable. Depending upon the probability of transfer, the mean life of the excited molecule may lie between the period of a single vibration ($\sim 10^{-13}$ sec) and the normal life of an excited state ($\sim 10^{-8}$ sec). In a cross-over, there is no change in the kinetic energy or position of the nuclei (Franck-Condon Principle), but there is a change in the potential energy, which gives rise to a vibrational mode. This vibrational energy is greater than the energy of dissociation. Accordingly, the molecule can dissociate into radicals after a single vibration (10^{-13} sec).

There are several processes, like predissociation, whereby the energy of excitation is transferred (in all or part) into generalized vibrational energy. Momentarily after the energy transfer occurs, the molecule is said to be thermally activated; that is, it is a "hot" molecule. To illustrate this, it has been calculated that a pentane molecule absorbing 100 kcal/mole from radiation will have a temperature of 6900°C above its original temperature 10^{-12} seconds after being struck. However, after 10^{-10} seconds the temperature has dropped to only 7°C above the original temperature. When the molecule is "hot" it can undergo chemical changes typical of thermal reactions, that is, reactions at high temperature. The molecule probably will dissociate into two radicals or into two stable molecules. An example of the latter is the decarboxylation of organic acids:



Processes in which electronic energy is converted into vibrational energy appear to be of dominant importance in determining the course of radiation-induced changes.

Collisions

An excited molecule may also lose energy by a collision of the second kind (non-radiation collision). The excited molecule can transfer its excitation energy into the electronic system, into the vibrational, or even into the translational energy of the collision partner. The bulk of the energy, however, will go into the electronic system.

Photon Emission

If no chemical process such as delayed dissociation or rearrangement takes place, an isolated excited molecule will have a mean life of not less than 10^{-9} second (average about 10^{-8} sec), and it will lose its energy of excitation by emitting a photon. Usually, this photon will have less energy than that of the absorbed radiation.

Cage Effect

The fate of an excited molecule can be profoundly influenced by its environment. A simple molecule, such as hydrogen iodide, HI, when dissolved in a chemically inert solvent can be photochemically dissociated just as if it were in the gas phase. However, the dissociated atoms will be caged-in by surrounding solvent molecules. Before they can escape this cage, the atoms will undergo many collisions with one another. As a result, there is considerable probability that they will recombine before they can separate. This Franck-Rabinowitch effect can be responsible for a noticeable decrease in the quantum yield of a dissociation process occurring in a solution. The probability of the escape from the cage is greater if the atoms are small and if they possess high kinetic energy.

Compared with simple molecules, complex molecules have a greater chance of losing energy because they have more atoms present to absorb energy in cage collisions. The activation energy necessary for a reaction increases with increasing molecular complexity. The radicals of complex molecules can rotate so that the reactive sites are no longer in the required definite orientation necessary for reaction. These effects prevent radical recombination in the cage and tend to counterbalance the lower kinetic energy due to size.

Migration

Excitation energy can migrate through many molecules in a crystal with strong binding forces and in which very good resonance exists between the neighboring fundamental units of the crystal. Migration plays only a minor role in molecular crystals.

7.1.2 Ionization

Reactions between ions and molecules are of importance in radiation chemistry. Except for the existence of the charge on one of the reactants, these reactions are in every way similar to the kinetic reaction steps of ordinary reactions. The recombination of ion-pairs may result in the formation of excited molecules. Since the energy of ionization exceeds that required for the dissociation of a chemical bond, it may be expected, in most cases, that dissociation will follow the recombination of an ion-pair. The behavior of some complex molecules, particularly aromatic hydrocarbons, is an interesting exception to this general rule.

Molecules can be ionized by impact with charged particles such as alpha particles, beta particles, protons, and electrons. Molecules are also ionized interaction with high-energy photons. In addition to impact ionization, a molecule containing high enough excitation energy may be spontaneously ionized by a process analogous to predissociation. This phenomenon is called preionization when it involves the valence electrons and the Auger effect when it is in the X-ray region. Molecules may also be ionized by thermal impact with an excited molecule or atom, provided the energy of excitation is greater than the energy of ionization of the molecule concerned. Also, two excited atoms can combine to form an ionized molecule and an electron. All of the preceding processes involve ejection of an electron and formation of a positive molecule-ion. Negative ions can be formed by the capture of an electron by a neutral molecule or atom.

That the primary action involves the individual atoms of a molecule should be kept in mind. However, it should be kept in mind that ultimately the charge always resides in the valence electrons and must belong to the molecule as a whole, not to a single constituent atom, except in special cases. However, there are differences in the distribution of charge in a molecule-ion characteristic of the particular energy state involved in the ionization. It is this average depletion of electron charge in a part of the molecule to which reference is properly made by the expression that a particular group or atom in the molecule is ionized.

7.1.3 General Summary-Excitation and Ionization

Charged particle and photon radiation interacts with organic molecules mainly through ionization and electronic excitation. The ions and excited molecules give rise to free radicals by charge neutralization and molecular decomposition. In radiation chemistry, those reactions which are known to proceed by free-radical mechanisms have been found to be predominant. Many investigators in the field of radiation effects believe that free radicals are the principal reaction-controlling intermediates.

There are cases in radiation chemistry in which the products are similar to those produced in thermal or photochemical reactions. The nature of the initial physical events affects the resultant chemical events. In thermal reactions, the energy is initially distributed over many degrees of freedom, and, in general, the most probable reaction is the one most favored by the frequency factor (probability) and particularly by the energy of activation. In photochemistry the process involving the lowest activation energy is not necessarily the most likely to occur. Also, the energy absorbed at a particular site may be converted to vibrational energy at some other site. This conversion permits the selective rupturing of one particular bond. In radiation chemistry, there appears to be a greater variety of possible products than possible with thermal or chemical reaction. This possibility undoubtedly is due to the fact that the primary excitation or primary ionization can occur anywhere in the molecule.

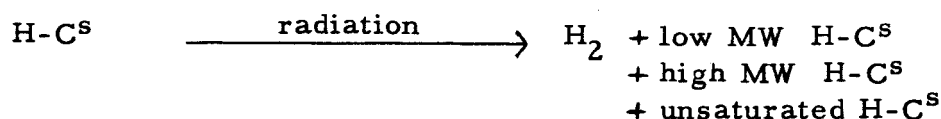
7.2 RADIATION CHEMISTRY OF HYDROCARBONS

Irradiation of Aliphatic Hydrocarbons

Aliphatic hydrocarbons are carbon-hydrogen containing compounds which have only a single bond (one electron pair) between any two bonded carbon atoms.

Both C-C and C-H bonds can be broken. The highly reactive fragments formed are capable of a variety of reactions including reaction with each other. If a foreign substance is present, the fragments can react with it, especially if it is a good acceptor. Oxygen and iodine are two examples of good acceptors.

General Reaction:



where: H-C represents any hydrocarbon
and MW represents molecular weight.

It is generally assumed that breakage of a carbon-hydrogen bond and subsequent cross-linking results in the formation of a compound having higher molecular weight than that of the original substance. Compared with the original molecule, cleavage of a carbon-carbon bond (chain scission) results in the formation of a lower molecular weight compound or of a slightly higher molecular weight compound via an end-linking process. All of the preceding discussion assumes that the reactive fragments do not recombine to form the original compound or react with a foreign substance. The theory is that the ratio of the probability of a C-C break to the probability of a C-H break is 0.36. Thus, the formation of high molecular weight compounds is favored.

When hydrocarbons are irradiated, the melting point goes down at first, then rises sharply until infusible gels are formed. An infusible gel is a high molecular weight compound which, when heated, changes to gaseous products and solid chars instead of changing to liquid form. The rate of double-bond formation has been found to be directly proportional to the dose, but reaches a maximum at high dosage.

Molecules containing branch chains are more susceptible to radiation damage than are molecules containing only straight chain groupings. Greater stability is observed with the higher molecular weight compounds.

The primary reactions are independent of phase; the secondary reactions are not. Both the product spectrum and the total yield varies with the phase. Greater mobility in the gaseous and liquid state should permit active particles to participate in more reactions than occur in the solid

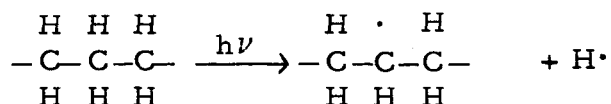
phase. In the liquid state, more radical recombination in the liquid "cage" and more collision-deactivation processes occur than in the gaseous state.

The introduction of an aromatic ring into an aliphatic compound increases the stability of the compound towards radiation. On the basis of evidence so far available, the stability appears to arise from a stabilization of the primary products of irradiation (ions, radicals, excited molecules), rather than stabilization of the molecule towards the attack of radicals formed in the primary act.

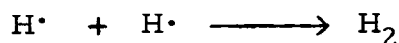
The predominant effect of the irradiation of aromatic hydrocarbons is the formation of polymers.

The fundamental reactions in which the radiation-produced free radicals serve an important function in hydrocarbons are given below.

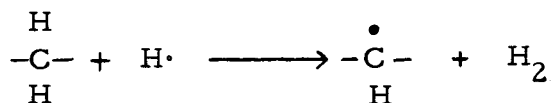
A. Formation of free radicals.



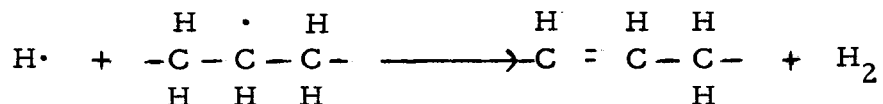
B. Combination of two hydrogen free radicals to form molecular hydrogen.



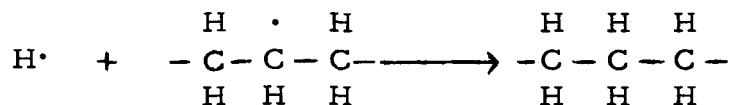
C. Hydrogen atom abstraction by a hydrogen free radical.



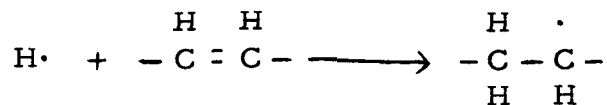
D. Double bond formation.



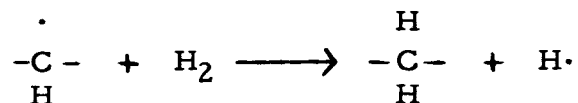
E. Radical recombination (reverse of reaction A).



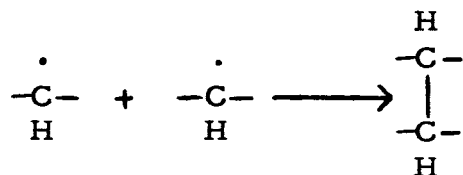
F. Double-bond elimination.



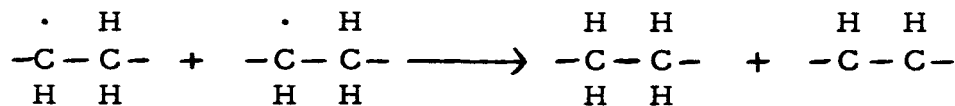
G. Reverse of hydrogen abstraction (reverse of Reaction C).



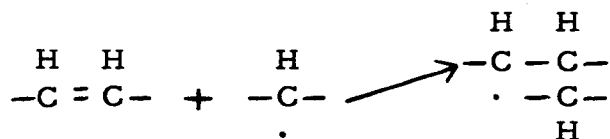
H. Cross-linking.



I. Radical elimination to form double bonds.

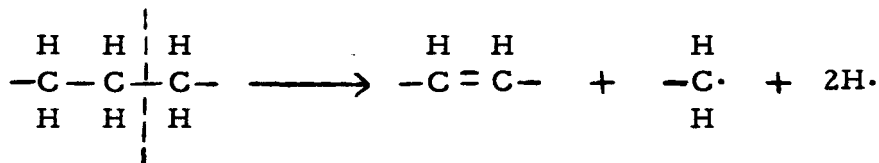


J. Reaction of double bonds leading to cross-linking.

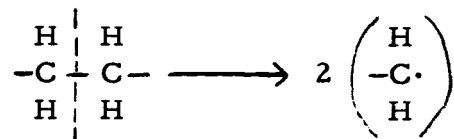


Reactions in which products are formed in a main carbon chain scission reaction are:

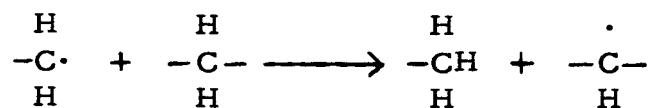
A. Formation of a double bond and a free radical.



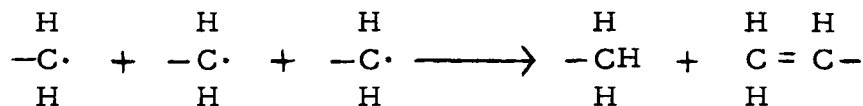
B. Free radical formation.



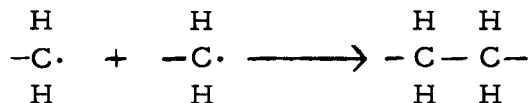
C. Hydrogen atom abstraction by free radical.



D. Combination of radicals to form double bonds.



E. Free radical recombination.



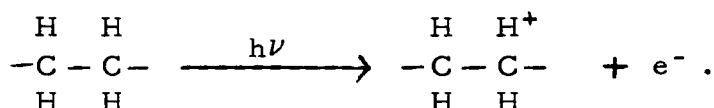
7.3 RADIATION DAMAGE PROCESSES IN ORGANIC MATERIALS

7.3.1 Photon ($h\nu$) and Electron Irradiation

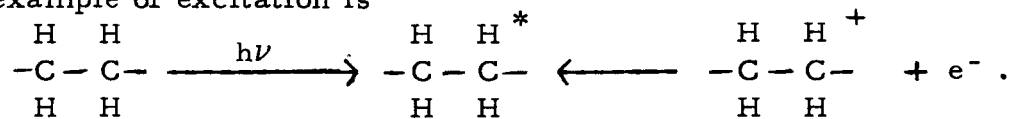
A knowledge of the energy transfer mechanisms is important in any explanation of radiation damage. The history of events associated with energy deposition is important in determining the type of reactions that take place. The absorbed radiation energy initiates primary processes such as atom recoil ionization and/or excitation which in turn produce secondary processes such as gamma emission, additional recoil atoms, photon emission, electron emission, etc.

Primary Processes

The two main primary processes for photon ($h\nu$) and electron irradiation are ionization and excitation. An example of ionization is



An example of excitation is



Photon irradiation

Electron irradiation

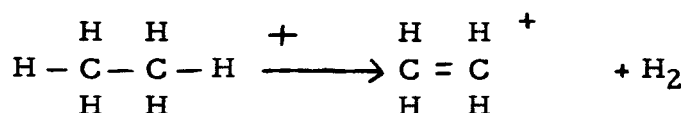
In the primary step, approximately one-half of the energy absorbed by an irradiated compound produces excitation, a process similar to that which occurs in photochemistry. The main difference between excitation produced by irradiation and that produced by monochromatic light is that the photo-excitation is usually specific while irradiation excitation is more general. That is, with photo-excitation, the same bond, group or excited state is initially involved in every activated molecule, while in irradiation excitation, a much broader range of excited states is possible. Thus, the irradiation-initiated reactions that can occur are much more numerous.

During irradiation, the conditions are such that almost any electronic orbital of the molecule may be involved. Thus, there may be a great variety of such states, and since high energy is available, it may be expected that these higher excited states will be present. Even though there are a great many excited states, there are also many processes through which energy can be transferred within the molecules and only a few or possibly only one electronic state may be involved in the chemical reaction step. In general, however, when compounds containing a variety of organic groups are irradiated, it may be expected that radiation-chemical excitations lead to a greater complexity of reaction than does photochemical excitation; e.g., radiolysis through excitation alone should give a greater variety of products than does photolysis.

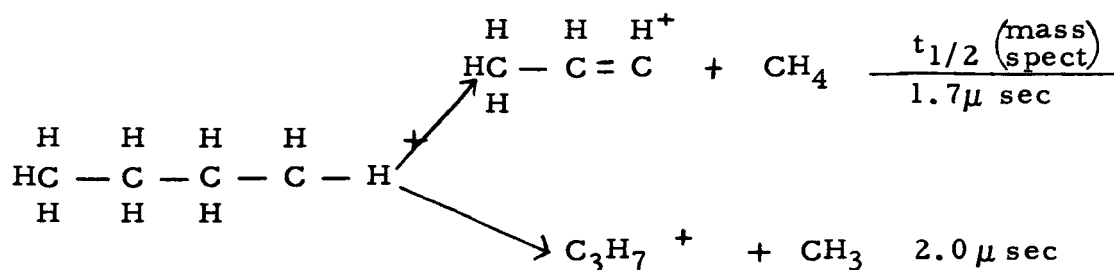
If the compound under irradiation is structurally complicated, there will be almost a continuum of excited states. The liquid state may permit the tapping-off of energy from upper excitation levels before these levels can make a chemical contribution. If there is a mechanism which requires some time between initial activation and chemical reaction, tapping-off of energy and internal conversion are almost certain to occur in the liquid state.

Secondary Processes

One of the secondary processes which may occur in the degradation of ionized molecules into smaller ionized species such as:



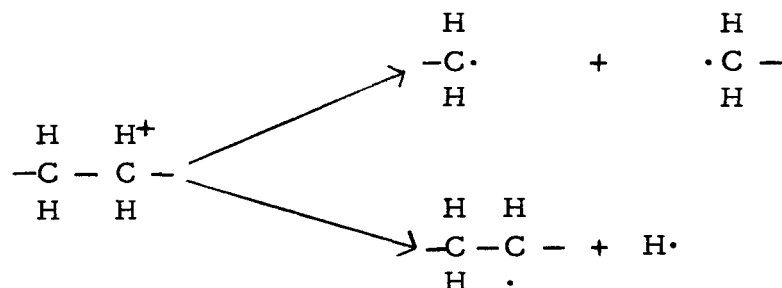
or



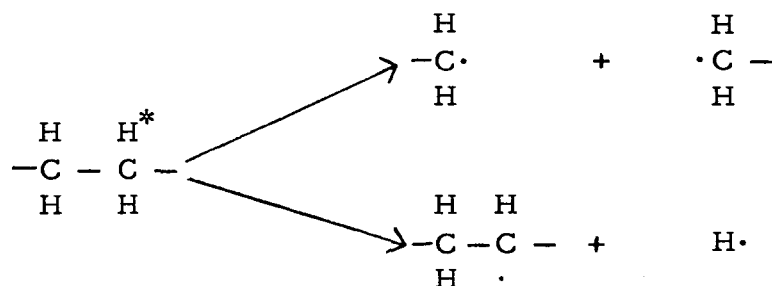
The activated species may undergo molecular rearrangement such as:



This type of secondary process may lead to many molecular species which were not present originally. Another secondary process is the decomposition of the excited and ionized molecules with the formation of free radicals such as:



or



7.3.2 Experimental Results

The G-value for an irradiated organic material is defined as the number of specified ions, atoms, radicals, or molecules changed or formed in the radiation process per 100 ev of energy absorbed by the system. (A negative G-value indicates that the number of entities decreases during the process - a high negative G-value for a reaction indicates polymerization.) G-values are useful in describing the processes which occur when a substance is irradiated.

During irradiation, saturated hydrocarbons give off hydrogen and some lower gaseous hydrocarbons. The type and amount of radiation-induced volatiles, however, depends on the phase of the irradiated sample as well as on the degree of saturation. There is some disagreement on the effect of chain length. Some investigators maintain that the G(gas) values (number of molecules of gas evolved per 100 ev absorbed) increase with increasing chain length while others hold that these G-values decrease with increasing chain length. The G(-m) values (in which -m indicates the number of monomers disappearing) for saturated hydrocarbons are very uniform (between four and eight) indicating that there is no chain polymerization and that the compounds are not particularly stable to radiation.

For the same amount of radiation energy absorbed, unsaturated hydrocarbons yield about one-fourth as much hydrogen as to saturated hydrocarbons. A slight amount of lower gaseous hydrocarbons are also evolved from unsaturated hydrocarbons. The G(-m) values for unsaturated hydrocarbons vary between 10 and 75, indicating that some chain polymerization takes place.

Organic halides are one of the most interesting classes of compounds to be irradiated in that there is a very good correlation between the processes that are observed when these compounds are irradiated and the bond energies for the various molecules. This correlation is demonstrated by the examples in Table 7.1.

TABLE 7.1
VARIATIONS IN OBSERVABLE CHARACTERISTICS¹

Type	Bond Energy	Observations upon irradiation
Fluorides	93.2 (kcal/mole)	No gas formation; C-C bond broken.
Chlorides	69.6 (kcal/mole)	No free Cl ₂ ; splits and H ₂ molecule.
Bromides	58.0 (kcal/mole)	Gaseous Br ₂ and HB _r more common.
Iodides	43.0 (kcal/mole)	Free I ₂ ; C-I bond broken.

¹ Huggins, Journal of American Chemical Society, Vol. 75 (1953), p. 4123.

The C-H bond strength is 87 kcal/mole and the C-C bond strength is 64 kcal/mole. The radiation-produced products of organic-halide compounds most closely conform to the accepted values for bond strengths.

Of all the hydrocarbons, the aromatic compounds are the most stable under the degrading influences of radiation. The aromatic compounds evolve very little gas and can absorb large amounts of radiation without breaking up. This stability is thought to be due to the energy sink formed by the resonance energy of the aromatic rings; the energy that the compound absorbs is distributed over the entire molecule.

7.3.3 Mechanism of Interaction with Particles and γ -Rays

Fast neutrons lose energy mainly through elastic collisions with atomic nuclei. In covalent organic materials, these collisions cause considerable damage. In hydrogenous organic compounds, this damage is induced primarily by hydrogen recoils. The fast neutron is scattered after colliding with the nucleus of a hydrogen atom, which then recoils and is ejected as a fast-moving proton. In hydrocarbons, this ejection leaves a negative ion (carbanion). In polyethylene, up to 95 percent of the fast-neutron damage can occur via this hydrogen-recoil mechanism. The fraction of the kinetic

energy of the neutron transferred per impact is given, on the average, by the relation $\Delta E/E = 2A/(A + 1)^2$, where A is the mass number of the nucleus which is struck and E is the kinetic energy of the neutron. For hydrogen (in which $A = 1$) on the average, half of the kinetic energy is lost per impact, but up to 100 percent of the energy may be lost in a single collision. When considering a single impact, the above relation must be modified to include the angle at which the molecule is struck.

Protons usually cause damage in organics by the same mechanisms as fast neutrons; however, in certain reactions the proton-damage mechanisms are similar to those of thermal neutrons. Deuterons are essentially heavy protons and they cause damage by mechanisms similar to those of protons. Very highly energetic alpha particles are heavy (mass = 4), strongly-ionized (charge = +2) particles which do damage by mechanisms similar to those of protons and deuterons.

The main source of thermal neutron damage in organic materials is by means of ionization by the 2.17 Mev gamma rays which are emitted when the neutrons are captured by hydrogen atoms. For a given neutron reactor source of thermal neutron intensity within a large volume of organic material, the intensity of the 2.17 Mev gammas resulting from capture by hydrogen can be approximately as high as the pile gamma intensity itself, and equivalent damage can result.

Since beta radiation consists of electrons or positrons emitted from nuclei, damage is caused by the same mechanism as the recoil (Compton) electrons produced by gamma radiation. Compared to fast neutrons, gamma rays and thermal neutrons, these beta-particles play only a minor role in radiation damage since they are produced in pile radiation on a much smaller scale, both in quantity and intensity. The mechanism of damage by high-energy electrons is similar to that by gamma and beta radiation. X-rays are generated by excitation of electrons in the innermost electron shells. Their mechanism of damage is similar to those of gamma, beta, and electron radiation.

The three most prominent methods of interaction of gamma radiation with matter are the photoelectric effect, the Compton effect, and pair production. The predominant interaction depends upon the atomic number of the constituents of the material and upon the energy of the gamma radiation. Most organic materials contain only elements of low atomic number and the photoelectric effect (probability $\propto \lambda^2 Z^3$) predominates for gamma energies below 0.1 Mev, the Compton effect (probability $\propto Z$) for energies from 0.1 to 10 Mev, and pair production (electron-positron) (probability $\propto Z^2$) above 10 Mev. For gamma rays of energies around 0.1 Mev, less than 3 percent of the ejected electrons are photoelectrons (possessing practically the same energy as the absorbed ray) and the mean energy of all the ejected electrons is slightly above 0.015 Mev. For 1 Mev gamma rays, almost all the ejected particles are Compton electrons and their mean energy approximates 0.440 Mev.

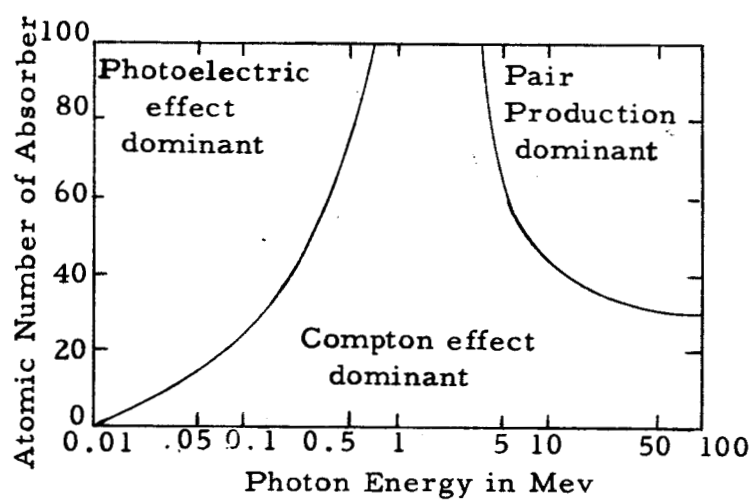


Fig. 7.2 - Energy ranges in which each of the three photon-atom interaction processes is the dominant energy transfer mechanism.

In the process of deceleration to usual room temperature energy (about 0.025 ev), an electron excites or ionizes many molecules along its path. For approximately each 30 ev of energy expended (by both primary radiation and secondary electrons), one ion-pair is produced. Again, approximately, only 15 ev is required to ionize a molecule. The remaining 15 ev is expended to exciting electron states of molecules. There will be two or three of these per ion-pair, depending on the height of the first excited electronic state above the ground state. Thus, in its deceleration to room temperature, a 0.440 Mev electron will produce about 15,000 ion-pairs and about two or three times as many excited molecules. The single molecule primarily affected by the gamma ray makes an imperceptible contribution to the over-all observed chemical phenomena.

We will now consider the approximate value of 30 ev quoted as the amount of energy expended per ion-pair produced. The value customarily given for air is 32.4 ev per ion-pair for electrons, X-rays, and γ -rays, and 35 ev per ion-pair for α -rays, protons, and neutrons. The value varies for different compounds; for example, the energy per ion-pair is 36.6 for ammonia and 26 ev for pentane. In gaseous organic systems a value of less than 30 ev is indicated and should be a realistic value. Very little is known about the energy required per ionization in liquids and solids. The approximate value of 15 ev quoted for ionization is realistic for organics. (Ionization potentials for several atoms are as follows: H = 13.595, C = 11.264, and O = 13.614 ev. The ionization potential of most organic compounds are in the range of 8 to 10 ev.) As was pointed out, there are two or three excitations per ion-pair formed. This corresponds to roughly 7.5 ev (170 kcal/mole) to 5 ev (115 kcal/mole) per excitation for two and three excitations, respectively. The bond strength for most organic bonds is approximately 80 kcal/mole. Obviously, if the energy of excitation can be applied to bond-breaking, enough energy is present from an excitation to cause cleavage of the usual organic bond.

The major difference between the effects of high-energy electrons and of high-energy heavy ions on matter results from their difference in velocity. Assuming equal energies and neglecting relativistic effects, a high voltage electron travels about 42 times faster than a proton, or 84 times faster than an alpha particle. These velocities affect the probability of interaction of the charged particle and the molecules of matter which it traverses. For example, it has been indicated that in a wet biological tissue of density 1 gram/cc (including the effects of secondaries), a 0.450 Mev electron will yield only about 2 ionizations per micron of path while a 1 Mev alpha yields about 5200 ionizations per micron of path and even a 10 kev alpha yields about 700 ionizations. Of course, the lighter particles will be more penetrating and this will tend to offset the large number of ionizations per unit path by the larger particles.

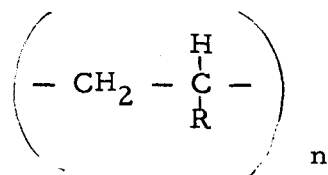
As already indicated, approximately half the absorbed energy is believed to be consumed in ionization processes and half in excitation processes. Most researchers believe that molecules excited (without ionization) by high-energy radiation behave as we might expect from our

knowledge of photochemistry, and that they make the anticipated contribution to the over-all chemical effect. In photochemistry, the activation is selective at some particular reaction site, while in radiation chemistry, the incident radiation may strike the molecule at any point and the energy will be transferred through the molecule to break a weak bond unless this is too difficult or involves a forbidden transition. Because of the similarity between reactions in photochemistry and radiation chemistry, we will now consider some of the ideas concerning energy exchange in photochemical reactions.

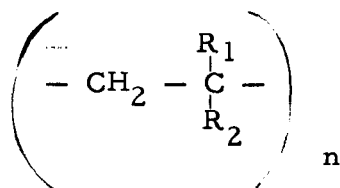
8. RADIATION EFFECTS IN POLYMERS⁵

Polymers either cross-link or degrade under irradiation depending upon their chemical structure. (1) The over-all effect of cross-linking is that the molecular weight of the polymer steadily increases with dose. When this occurs the polymer no longer melts at temperatures above its normal melting point. When treated with their usual solvents they do not completely dissolve but rather a swollen gel fraction is left as a residue. The degree of swelling of the gel steadily decreases with dose. (2) In degradation the polymer suffers random chain scissions and the molecular weight steadily decreases with dose. In some cases the final product is a LMW liquid. Degradation proceeds through a single-step process and the yields of degradation are generally low.

Both cross-linking and degradation may occur simultaneously in the same polymer. If cross-linking occurs at a higher yield rate than degradation the net result is cross-linking; if the converse is true the net result is degradation. None of the theories advanced to explain why some polymers cross-link and others degrade are completely satisfactory. However, a general empirical rule is that when the structure of a vinyl polymer is such that each carbon atom of the main chain carries at least one hydrogen atom, the polymer cross-links under irradiation, but if a tetrasubstituted carbon atom is present in the monomer the polymer degrades under irradiation. Hence polymers with the structure



will cross-link (Group I) and those with the structure



will degrade (Group II). Steric repulsion as a consequence of the presence of the tetrasubstituted carbon in the chain of Group II polymers is believed to weaken the C-C bond in the main chain. (Heat of polymerization data) This feature also strongly affects the thermal stability of a polymer. With a few exceptions, polymers which degrade under irradiation are also those which yield the largest proportion of monomer when heated in vacuum.

8.1 CROSS-LINKING POLYMERS

The formation of intermolecular cross-links is one of the most important chemical changes brought about by irradiation in polymers of Group I. Cross-linking of many polymers leads to beneficial changes in

heat resistance
tensile strength
cold flow.

We will restrict the discussion to polyethylene. It is believed that some of the conclusions reached in the exhaustive study of polyethylene can be extended to other polymers in Group I.

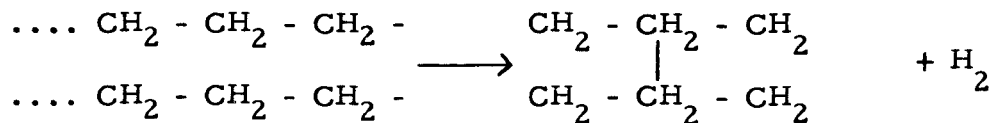
Polyethylene is partially crystalline at temperatures below 110° - 115°C . The chemical changes produced in polyethylene by irradiation are basically similar to the chemical modifications observed in the radiolysis of low-molecular weight paraffins. As in the paraffins the molecular structure may affect radiation-induced changes in polyethylene.

In vacuum reactor irradiation produces weight loss in polyethylene films owing to the evolution of hydrogen and low-molecular-weight hydrocarbons. Double bonds are formed in this process (infrared data). In air, however, the weight of polyethylene increases during reactor irradiation. Carbonyl and carboxyl groups were formed (infrared data). In vacuum, the tensile strength increased; in air it decreased.

Polyethylene becomes cross-linked during reactor irradiation (Pre-irradiated $\text{DP} = 2.5 \times 10^4$).

1. Up to 4.5 megarads only slight cross-linking occurs.
2. After 4.5 - 900 megarads it becomes a partly insoluble polymer. The gel-fraction increases with dose. Above 110°C it becomes transparent.
3. For doses above 900 megarads it becomes heavily cross-linked and is a dark-tinted transparent glass. Hard and very brittle.
4. Irradiated in air it shows an oxygen rich wax-like surface film.
5. 98% of gas liberation is hydrogen.

Cross-linking believed to proceed as follows:

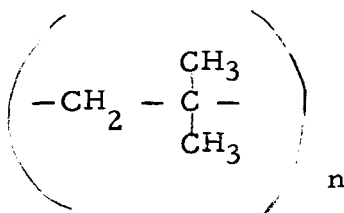


Hence hydrogen evolution is a measure of cross linking.

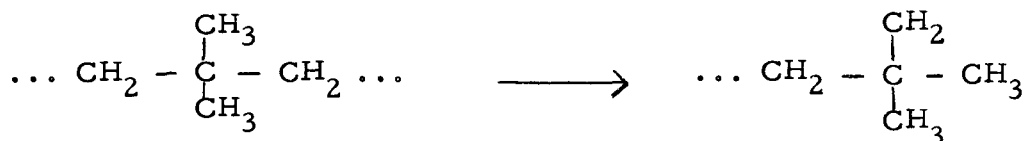
8.2 DEGRADING POLYMERS

Polyisobutylene is perhaps the simplest polymer of the degrading type, since its structure is that of a branched hydrocarbon chain having one

tetrasubstituted carbon atom in its monomer.



Degradation appears to proceed when the activated polymer molecule can rearrange in such a way as to give two stable molecules. Hence in polyisobutylene



is one degradation mechanism. Note this mechanism does not indicate hydrogen evolution.

8.3 GENERAL COMMENTS

The most important modifications observed in irradiated polymers, i.e., cross-linking and degradation are closely related to the condensation and scission reactions produced in low-molecular-weight organics. Gas evolution, and double-bond formation also occur with comparable yields in polymers. A major difficulty encountered in polymer irradiation studies is the fact that one is dealing with chemical reactions in the solid state. Relatively little is known about this process.

The most radiation-resistant polymers appear to be those containing aromatic substituents. Polymers which degrade, rapidly lose mechanical strength and for large doses crumble into powder (Teflon) or become sticky (polyisobutylene) and go into a viscous liquid. Elastomers lose elastic properties for doses $\sim 10^8$ rads, especially if exposed to oxygen. Teflon appears to degrade to a large degree due to oxygen.

Mechanical property changes are significant only for doses exceeding $10^6 - 10^{10}$ rads. Degrading polymers lose strength above 5 megarads. Teflon breaks down mechanically at 5×10^4 rad. Loss of mechanical strength arises from the formation of LMW products which act as plasticizers.

Cross-link polymers show elastic modulus increase for doses above $10^7 - 10^8$ rads.

Gases are evolved during irradiation of all polymers. Internal strains due to gas buildup can lead to disintegration. These effects are often delayed, occurring months after irradiation.

When a linear polymer becomes cross-linked, it no longer melts but becomes rubber-like at temperatures above the normal softening point. The increase in elastic modulus above the softening point is a very sensitive measure of the degree of cross-linking caused by irradiation.

Color changes occur above 10 megarads. These are thought to be due to

formation of conjugated double bonds
trapped free radicals
trapped ions.

Electrical conductivity increases several orders of magnitude.

All polymers evolve gas under irradiation. The initial gas yield is larger than the yield for longer times. This suggests that precursors of gaseous products are involved in secondary processes with active groups (free radicals) during long irradiation.

Double bond formation seems to be proportional to the number of main chain scissions in degradation. The effect of oxygen is sufficiently strong to cause degradation when a polymer that cross-links in vacuum irradiation conditions will degrade when irradiated in air. In bulk specimens effects of oxygen are less pronounced since the oxidation process is then diffusion controlled, unless the dose is sufficiently low that the oxygen infusion rate is larger than the rate of oxygen consumption in oxidation of radiation products.

Free radicals are trapped within crystalline regions or in viscous regions produced by irradiation.

A gel is an infinite three-dimensional network of polymer molecules. An analysis of gel formation and post-gel reactions is useful in radiation damage studies.

9. ANTI-RADS^{4, 5}

Any element or compound added to a material that improves the resistance to radiation damage is called an "anti-rad." It is quite possible to have an anti-rad which is deleterious to one property while it enhances another more desirable property. Organic compounds do not withstand high temperatures or radiation very well because their interatomic bonds are weak, in the range 50 - 100 kilocalories per mole. On the average, 80 percent of the absorbed radiation energy goes into heat and 20 percent into bond breakage. About 25 ev are absorbed per bond broken. Thus,

$$\frac{10^{23} \frac{\text{bonds}}{\text{gram}} \times 25 \frac{\text{ev}}{\text{bond}} \times 1.6 \times 10^{-12} \frac{\text{ergs}}{\text{ev}}}{90 \frac{\text{ergs}}{\text{gram roentgen}}} = 0.44 \times 10^{11} \text{ roentgens}$$

is theoretically required to break all the bonds per gram of material. Usually, however, the breaking of 1 percent of the bonds will change the properties significantly. Thus, only 4×10^8 roentgens are needed to significantly change the properties of an organic material. In general, anti-rads are used to protect organic materials, but their use in some inorganic materials can be cited.

Anti-rads may be used to lessen bond breakage or to minimize the reactions of those bond-breakage products which produce undesired properties.

Three considerations are involved in selecting an anti-rad:

1. Properties of organic materials are dependent upon molecular structure and orientation.
2. The reaction types which change molecular structure and thereby degrade or improve a desired property must be known if one is to control them specifically and efficiently by the use of additives.
3. The particular anti-rad used to control a reaction type necessarily depends on the reaction mechanism involved.

Nucleophilic agents (electron pair donors) are used to prevent oxidation (in the general sense) of the primary material. Among those used are:

1. Quinhydrone
2. Pyrogallol
3. Hydroxylamine hydrochloride
4. Cysteine

Electrophilic agents (electron pair acceptors) are used to prevent reduction of the primary material. This class includes:

1. Iodine
2. Bromine
3. Potassium permanganate
4. Hydrogen peroxide

Aromatic ring systems may act as "energy sponges." They have sufficient resonance energy to hold together long enough for the absorbed energy is dissipated as heat. A side group greatly increases their anti-rad efficiency by acting as a "point of entry" for the energy. A few examples are:

1. Terphenyl
2. Ethyl benzene
3. p-Amino benzoic acid
4. Biphenyl amine

Stable free radicals provide protection for a primary material by "taking up" free radicals or activated molecules produced by radiation, thus preventing further chemical reactions.

Examples are:

1. α - α' - diphenyl β - picryl hydrazyl
2. Triphenyl methyl
3. S-2-amino ethyl isothio uronium

If a molecule has been equipped with a weak bond located in a non-critical place, the energy from absorption of radiation most likely will go into breaking this unimportant bond rather than an important one.

For example:

1. C-I side bonds on a C-C-C chain
2. C-S instead of C-F or C-C-C

Properties dependent upon cross-linking may be promoted in polymers under irradiation by the addition of compounds such as:

1. p-Divinyl benzene
2. Sulfur
3. Organic peroxides

There are substances which readily form rings. Chelation compounds are an example. Typical ring formers are:

1. Phenylene diamine
2. Ethylene diamine
3. Benzyl methyl glyoxime
4. Salicyl aldehyde

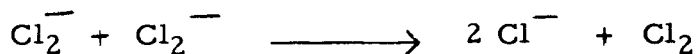
Agents known as "fillers" may reduce radiation damage in elastomers and other polymers. One possible mechanism is surface catalysis of recombination reactions. Also surface absorption of electrons or ions may be involved. Commonly used fillers are:

1. Asbestos
2. Mica
3. Zinc oxide
4. Lead dioxide
5. Carbon black

Energy absorbed from radiation may be released in the form of fluorescence rather than going into bond breakage or being released as heat. Specific elements and compounds "activate" this form of energy release. Examples are:

1. Thallium
2. Manganese
3. Oxazoles

Catalysts which promote chain-termination reactions when chain reactions are possible or probable or catalysts which favor the reverse or recombination reaction will act as anti-rads in some situations. For example, in the iron-induced chain reaction between chlorine and oxalic acid the chain-breaking step



is catalyzed by VO^{++} . Undoubtedly some of the fillers act in this manner.

From the above listing one may observe that an anti-rad agent may act by more than one mechanism. For example, diphenylamine is an energy sponge, a reducing agent, and a ring former. Sulfur may be a weak-side-chain breaker, a reducing agent, a cross-linker and a ring former.

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